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Screening Methods for PAH (Polynuclear Aromatic Hydrocarbon) Priority Pollutants in Wastewater

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SCREENING METHODS FOR PAH PRIORITY POLLUTANTS IN WASTEWATER

by

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A screening method for the determination of total polynuclear aromatic hydrocarbon (PAH) concentration in industrial effluents was developed. The method employs solvent extraction, alumina column chromatographic cleanup, and UV absorbance determination. The UV detection step utilizes a bandpass filter in order to obtain more uniform response between the various PAHs.

The PAH screening method results and U.S. EPA Method 610 results have been found to be positively correlated for a variety of industrial wastewater samples. The screening method can be performed in approximately one-half to one-third the time required for U.S. EPA Method 610 and requires considerably less expensive equipment.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

Under authority of Sections 304(h) and 501(a) of the Federal Water Pollution Control Act of 1972 and the Clean Water Act of 1977, the Environmental Protection Agency is required to promulgate guidelines establishing test procedures for the analysis of pollutants. This report represents the state-of-the-art for the measurement of total polynuclear aromatic hydrocarbons (PAH) in industrial wastewaters.

Robert L. Booth

Robert L. Booth, Acting Director
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ABSTRACT

A screening method for the determination of total polynuclear aromatic hydrocarbon (PAH) concentration in industrial effluents was developed. The method employs solvent extraction, alumina column chromatographic cleanup, and UV absorbance determination. The UV detection step utilizes a bandpass filter in order to obtain more uniform response between the various PAHs.

The PAH screening method results and U.S. EPA Method 610 results have been found to be positively correlated for a variety of industrial wastewater samples. The screening method can be performed in approximately one half to one third the time required for U.S. EPA Method 610 and requires considerably less expensive equipment.

This report was submitted in partial fulfillment of Contract No. 68-03-2984 by Battelle Columbus Laboratories under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period September 12, 1980 to May 15, 1981, and the work was completed as of June 15, 1981.

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SECTION 1

INTRODUCTION

The objective of this program was to develop a simplified group test procedure or "screening method" for determining polynuclear aromatic hydrocarbon (PAH) priority pollutants in aqueous samples. This method is designed to serve as an indicator of pollutant level which can be employed in conjunction with the more specific U.S. EPA Method 610, previously developed by the U.S. EPA for determining individual PAH priority pollutants in industrial wastewater. A listing of the priority pollutant PAHs is given in Table 1. The use of such methods will be especially useful for screening samples to determine whether the pollutant levels are relatively high or low.

The requirements which such screening methods are expected to meet are given below:

(1) Quantification shall be positively correlated to that produced by the refined Section 304(h) Clean Water Act methods (as the sum of the individual pollutants).

(2) The methods shall be able to stand alone as reliable indicators of pollutant level.

(3) The cost shall be no more than one-half of that using the refined 304(h) gas chromatographic (GC) or combined gas chromatography/mass spectrometry (GC/MS) methods.

(4) Response shall be class specific, producing a very low frequency of false responses.

(5) Responses need not be produced for individual pollutants. Quantification may be based on a unified response of the category.

(6) Quantification shall produce a numerical value (rather than a range).

(7) Detection limit shall be at least 1 μg/L.

(8) Recovery shall be 70% or greater for the priority pollutants in the category.

TABLE 1. PRIORITY POLLUTANT PAHs

Naphthalene
Acenaphthalene
Acenaphthene
Fluorene
Anthracene
Phenanthrene
Pyrene
Fluoranthene
Benzo(a)anthracene
Chrysene
Benzo(k)fluoranthene
Benzo(b)fluoranthene
Benzo(a)pyrene
Dibenzo(a,h)anthracene
Benzo(ghi)perylene
Indeno(1,2,3-cd)pyrene

(9) The relative precision (as relative standard deviation) of replicate determinations shall be less than 50%.

(10) Ruggedness shall be maximized.

(11) The cost of the instrumentation required for the methods shall not exceed $10,000.

The major objective of this program was to select, evaluate, and validate the method which best meets the requirements listed above for the priority pollutant PAHs. To accomplish this objective, a literature survey was conducted to formulate the most logical approach to meet these goals. Three candidate approaches (thin-layer chromatography, fluorescence and UV absorbance) were selected for laboratory evaluation.

SECTION 2

CONCLUSIONS

The total ultraviolet (UV) absorbance method was selected as the method of choice for the PAH priority pollutants in wastewater. This method has been demonstrated to be simpler and more reliable than a PAH detection method based on fluorescence measurement or a thin layer chromatography (TLC) spot test. The method requires a factor of two to three less time to conduct than U.S. EPA Method 610. In particular, the sample extraction, instrument calibration, sample analysis, and data interpretation steps are conducted more quickly for the screening method than for U.S. EPA Method 610. In addition, the screening method requires less expensive equipment (~$5,000) than does U.S. EPA Method 610 (~$25,000).

Recovery of individual PAHs using the screening method extraction and cleanup steps were better than 75% with the exception of benzo(k)fluoranthene, which was 40-50% at both high and low spike levels. The total PAH value obtained using the screening method is consistantly higher than the value obtained using U.S. EPA Method 610. This positive bias (approximately 30%) is due to the use of fluoranthene as the PAH equivalent standard which has a molar absorptivity slightly less than the average molar absorptivity of the 16 PAH compounds spiked.

While this bias can be significantly reduced by selecting a different PAH calibration standard, this procedure would not be applicable in a real world situation, i.e., when the concentration and type of PAHs present is not known. In practice, the amount of bias will not be known and will vary from sample to sample, within the relative sensitivity factors of the various PAH compounds (i.e., ±100% relative to fluoranthene). In certain cases where the major PAH species is known, the amount of bias can be minimized by calibrating with that particular PAH species.

A limited number of wastewaters were evaluated by the total UV absorbance method (a POTW secondary effluent, a coking process effluent, and a refinery effluent). All wastewaters were found to contain PAHs when analyzed by U.S. EPA Method 610 as well as by GC/MS. Comparison of the data obtained using the screening method to that obtained using U.S. EPA Method 610 indicated a positive bias as described above. Nevertheless, the screening method clearly indicated the presence of PAHs at the appropriate concentration levels, and the data for all samples using U.S. EPA Method 610 and the screening methods showed a firm positive correlation. GC/MS analysis of several extracts indicated the presence of PAHs as well as low levels of dioctylphthalate (DOP). Methylthiobenzene was found in the refinery effluents. While the cleanup procedure removes phthalates, the sample extracts may have been contaminated with DOP following the cleanup procedure. However, neither DOP nor methylthiobenzene represent substantial interferences in the screening method because of low concentration and low molar absorptivity compared to the PAHs. This conclusion is confirmed by the lack of substantial positive bias in the screening method value for the unspiked refinery effluent.

Nevertheless, judgment must be exercised as to the source of the wastewater and potential type of contaminants which could be present. In general, the total UV absorbance method has the ability to stand alone as a reliable indicator of pollutant concentration. However, if necessary, this procedure can be used in conjunction with compound specific procedures (e.g., U.S. EPA Method 610 using high performance liquid chromatography (HPLC) or U.S. EPA Method 625 using GC/MS). For example, extracts generated by the U.S. EPA Method 610 workup procedure could be analyzed using the total UV method prior to HPLC analysis in order to eliminate low level samples from further consideration, thereby reducing analytical costs.

SECTION 3

RECOMMENDATIONS

The screening method for PAHs developed in this study should be applied to industrial wastewaters from various processes which would be expected to emit PAHs. The results obtained using the PAH screening method should be compared to the results obtained using U.S. EPA Methods 610 (HPLC) and/or 625 (GC/MS) in order to determine if the screening method is a reliable indicator of total PAH concentration in the particular matrix of interest. Although a strong positive correlation has been found between U.S. EPA Method 610 and the screening method for POTW effluent, refinery effluent, and coking process effluent, there may be matrices which contain substantial quantities of positive interferences (i.e., compounds which are not removed by alumina chromatography and absorb UV radiation). Since negative interferences are highly unlikely using the screening PAH method, this method can be applied as a reliable indicator to determine whether further analysis (e.g., GC/MS or HPLC) is required. The method also can be used to rapidly compare pollutant concentration in a stream as a function of time to assess the variability in stream composition.

The development of screening methods for other classes of pollutants (e.g., nitrosamines) should be considered since such methods can reduce analytical costs substantially.

SECTION 4

LITERATURE REVIEW

The priority pollutant PAHs as a class have the common properties of high UV absorbance and high fluorescence quantum yield, which are useful for developing a class specific method. The low water solubility of these compounds permits solvent extraction from the aqueous matrix and the high fluorescence and UV absorbance of the PAHs facilitate detection at relatively low levels.

The extraction of PAHs from aqueous matrices can be achieved by several techniques. Solvent extraction (hexane, methylene chloride, chloroform), absorption on macroreticulate resins (XAD-2, XAD-4) and retention on reversed phase column packings (Waters C-18 SEP-PAK® Cartridges) have all been suggested. Based on published extraction studies (1-2), it appears that the existing methylene chloride extraction procedure of U.S. EPA Method 610 is more direct, efficient, and less time consuming than the alternative techniques which have been reviewed.

The cleanup procedures selected for further investigation are critical, since the specificity obtained in this step determines the degree of precision and accuracy of the measurement step. Several preparative techniques have been found to be effective. Gel permeation chromatography using a variety of column packings has been suggested (2,3,4). Sawacki, et al. (5) suggested column chromatography using an activated alumina column for PAH isolation. These approaches are similar in nature to the silica gel column chromatographic technique of U.S. EPA Method 610. They offer neither decreased cost nor decreased analysis time. However, very recent research at Battelle (6) indicates that the activated alumina column cleanup offers increased selectivity compared to the silica column cleanup, especially for the removal of polychlorinated biphenyls (PCBs).

Various HPLC procedures have been suggested for the class separation of PAHs from other organics (7-9). The application of a μ-Bondapak-NH_2 column (aminopropylsilane bonded to 10 μm porous silica) for the separation of PAHs by ring number from interferences has been reported by Wise, et al. (9). However, such approaches are relatively time consuming and require moderately sophisticated equipment.

A second chromatographic technique which has been widely investigated is TLC (10-16). This technique has been used for both preparative and analytical work, using a variety of substrates, including polyamide (10), organo-clay (12), acetylated cellulose (14), alumina (13), and silica gel (16). Most methods involve separation of individual PAHs and require further sample preparation (e.g., scraping material from the TLC plate). The method of Zoccolillo and Liberti (16), however, is a direct measurement of total PAHs. A sample extract is separated on silica gel plates on which narrow channels have been defined. The total amount of PAHs is determined by measuring the length of the developed band, visualised using a hand-held UV source.

The sensitised PAH spot test of Smith and Levine (17), while being a useful tool for screening samples for approximate levels of PAHs, appears to have limited usefulness for the quantification of PAH in environmental samples due to the wide variation in response for different PAHs and high susceptibility to interference (18-19). In its current form, the determination of naphthalene is not feasible since this PAH is used as the sensitising agent. Review of the literature suggests that regardless of the sensitiser, the possibility of precise quantification using such a visual comparison technique is remote.

The preferred methods of detection for use with all of the above techniques are UV spectrophotometry and fluorescence. Both of these have been applied to a wide variety of samples. Direct UV absorbance measurements are particularly applicable to organic extracts, although the selectivity of the cleanup procedures can greatly affect the results. Characterisation of the PAHs in marine and freshwater samples is described by Chesler, et al. (7) and Levy (20). Instead of the commonly used measurement at 254 nm, Grant and Meiris (12) monitor the UV absorbance at four specific wavelengths, 300 nm, 330 nm, 385 nm, and 430 nm, in order to overcome the differences in absorbance maxima of various PAHs.

Direct fluorescence measurments have also been quantitatively applied to a variety of samples including marine (21) and freshwater (22), shale oil (23), and coal products (24). Direct fluorescence has been used to identify and quantify PAHs on TLC plates as well as in organic extracts. Having high fluorescence quantum yields, PAHs can be measured at very low concentration levels (1 μg/L), provided that interferences have been removed.

One difficulty with direct fluorescence measurements is the variability of the fluorescence intensity of various compounds at specific wavelengths. This problem could possibly be resolved using an approach similar to that of Grant and Meiris (12) wherein several excitation and emission wavelengths are selected. Another approach to the problem is synchronous scanning fluorescence spectroscopy (24-26). However, the equipment sophistication required precludes it from consideration as a screening method.

Based on this literature survey and discussions with several experts, the following approaches were recommended for investigation as candidate PAH screening methods.

EXTRACTION AND CLEANUP

The extraction and cleanup procedure of the U.S. EPA Method 610 was recommended for use with slight modifications because PAHs can be isolated very efficiently from wastewater using this approach. However, the separation of the PAHs from the non-polar benzenes and PCBs is rather poor using silica gel cleanup. Since these compounds can interfere with a UV detection method, it was considered worthwhile to replace the silica gel cleanup step by an activated alumina column cleanup procedure, to improve method selectivity. A single extraction, rather than triplicate extraction with methylene chloride was recommended in order to streamline the screening method.

TOTAL UV ABSORBANCE METHOD

The simplest method and the one ultimately selected as the PAH screening method is the measurement of total UV absorbance. This method avoids the problem of different responses for individual PAHs at a specific wavelength measurement. For this method, a very inexpensive instrument is required consisting of a deuterium lamp as a UV light source (∿200-350 nm), a bandpass filter which blocks wavelengths below ∿240 nm to remove contributions from the solvent, a cuvette to contain the isolated PAH extract, and a photodetector.

DIRECT FLUORESCENCE METHOD

The approaches used for fluorescence measurements were similar to those used for absorption measurements (i.e., total fluorescence using broad bandpass filters). Advantages of fluorometry over UV spectrometry are higher sensitivity and high selectivity (non-fluorescent potential interfering compounds are not detected). A disadvantage is that the sensitivity for naphthalene will be lower than for other PAHs because it absorbs and fluoresces at lower wavelengths. In addition to total fluorescence measurement a spectrofluorometer can be used to obtain measurements at several specific wavelengths, to partially overcome the variability in response among the various PAHs.

CHANNEL TLC METHOD

Zoccolillo and Liberti (16) describe a TLC method using very narrow channels on a silica gel TLC plate. PAHs are eluted as a single band and the length of the band is related to the total PAH concentration. This procedure is actually the TLC equivalent of the total UV measurement method which is described above. The method employs a single wavelength UV source as the visualization technique, and incorporates its own cleanup step thus requiring only sample extraction and concentration. The variability in response between various PAHs is expected to be quite large, thus making quantification more difficult.

SECTION 5

EXPERIMENTAL PROCEDURES

EVALUATION OF FLUORESCENCE DETECTION

All fluorescence measurements were conducted using a Perkin-Elmer Model MPF-44B Spectrofluorometer. This instrument is equipped with grating monochrometers and adjustable slits on both the excitation and emission beams. Both gratings can be adjusted to zero order, allowing white light to be transmitted. By adjusting the grating zero order and placing an optical filter in the beam the instrument can be used as a filter fluorometer.

All experiments were conducted using distilled-in-glass solvents and reference standards of highest purity available. All reference materials were assayed by high performance liquid chromatography with UV and fluorescence detectors, using the conditions specified in U.S. EPA Method 610. Chrysene was purified by column chromatography on silica gel to remove a polar fluorescent impurity. All PAH reference standards for evaluation of fluorescence detection were prepared in cyclohexane. Quinine sulfate, used as a fluorescence reference standard to ensure proper instrument performance, was prepared in 0.1 N sulfuric acid.

The spectrofluorometer was operated in the ratio mode for all experiments. This mode of operation corrects for variations in lamp intensity. The response was generally set at 1.2 and the amplifier gain was adjusted to obtain a non-saturated signal.

The results of specific experiments performed using the spectrofluorometer are described in Section 6.

EVALUATION OF UV DETECTION

UV spectra for 14 of the 16 PAHs were obtained from literature sources (27) and the average molar absorbance over specified wavelength ranges were calculated. These data were used to select appropriate wavelength ranges, to be employed in laboratory experiments, which would give the least compound to compound variability in response.

Absorbance measurements were performed using a Perkin-Elmer Model 55B UV spectrophotometer with a Coleman Model 55-204 UV accessory deuterium lamp. By setting the wavelength dial to zero (000 reading) the instrument grating becomes zero order and can be used for total UV absorbance measurements, wherein an optical filter is placed in the beam to select the wavelength region.

A bandpass filter (Corning CS 7-34) and a cutoff filter (Corning CS 9-54) were evaluated using the above instrumentation. The UV transmittance characteristics of these two filters are shown in Figures 1 and 2. Apparent molar absorptivities ($\bar{E}$) and detection limits using standard PAH solutions (in cyclohexane) were determined for both filters.

Conventional 1 cm x 1 cm quartz cuvettes were employed for most of the experiments, although self-masking microcuvettes (0.2 cm x 1 cm) were employed for wastewater extracts, in order to reduce the volume of sample extract required.

The instrument baseline level was set to zero using pure cyclohexane just prior to each set of sample analyses and was checked periodically throughout a given analysis sequence. Unless otherwise specified, all measurements were conducted using cyclohexane solutions of the PAHs.

EVALUATION OF COLUMN CLEANUP APPROACHES

Various column cleanup approached were investigated for use in conjunction with a UV or fluorescence determinative step. Alumina (Fisher Absorption Alumina, 80-200 mesh) and silica gel (Davidson Grade 923, 100-200 mesh) were evaluated. Alumina was activated by heating for 12 hours at 450°C and stored in a tightly capped glass bottle for no more than 48 hours before use. Silica gel was activated by heating for at least 12 hours at 160°C and was stored uncapped in the oven at 160°C when not in use.

Chromatographic columns (10 mm x 250 mm) were packed as a methylene chloride slurry by pouring the slurry into the column with the stopcock open. The remaining adsorbent was rinsed into the column with methylene chloride (~10 mL) and subsequently the column was rinsed with 2 mL, 3 mL, and 35 mL of pentane. When the pentane level reached the head of the column the flow was stopped and the sample applied. All subsequent elution steps were conducted using a solvent flow of approximately 2 mL/minute.

The performance of the column cleanup procedures, in terms of selectively removing potential interferences, was evaluated using standard solutions containing polar and non-polar components. The particular compounds evaluated were selected on the basis of the likelihood of finding such materials in the environment and the potential for interferences with PAH (e.g., only UV absorbing compounds were evaluated). These solutions were designated ST INTF 1 (non-polar components) and ST INTF 2 (polar components).

ST INTF 1 contained hexachlorobenzene, 1,2,4-trichlorobenzene, 2,2',4,4',6,6'-hexachlorobiphenyl, 2,2',4,4'-tetrachlorobiphenyl, and 1,2,4-trimethylbenzene. ST INTF 2 contained pyridine, indole, quinoline, carbazole, acridine, dibenzo(a,j)acridine, benzo(f)quinoline, benzo(h)quinoline, benzothiazole. Dioctyl phthalate (DOP), dibenzothiophene, and 2,6-dibutylphenol were included along with the polar ST INTF 2 components in certain cases. The ST INTF 1 and ST INTF 2 solutions contained 100 mg/liter of each component in cyclohexane.

Elution characteristics of PAHs were investigated using an equimolar mixture containing all 16 PAHs in cyclohexane. Elution characteristics of the various components were determined by analyzing the chromatographic fractions using either a UV method (identical to the determinative step in the method presented in Appendix B) or by gas chromatography using the following conditions:

Instrument - Carbo Erba Model 2160
Column - 30 meter SE-52 glass capillary
Flow - 2 mL/minute helium
Detector - FID
Column Temperature - 80-250°C @ 4°C/minute
Injection Volume - 2 µL split 10:1
Detector Temperature - 300°C
Injector Temperature - 250°C

Recoveries were determined by comparison of UV absorbance and/or GC peak area to a reference standard, having a concentration representing 100% recovery. When necessary to achieve better sensitivity, the chromatographic fractions were concentrated to 1 mL final volume using a Kuderna-Danish evaporator equipped with a microSnyder column.

EVALUATION OF THIN LAYER CHROMATOGRAPHIC METHODS

The channel TLC approach (16) was evaluated to determine whether or not it could be used as a screening method for PAHs. This approach involved spotting the solution to be analyzed on a thin channel TLC plate and measuring the length of the PAH spot after elution. Literature reports (16) indicate that spot length can be related to concentration in some cases.

Silica gel and alumina TLC plates 20 cm x 20 cm were obtained from Analabs, Inc. The alumina plates Type HF, and silica gel plates Type AGF, were impregnated with a fluorescence indicator. Both types of plates had a thickness of 250 microns. Plates were scored with 3 mm wide channels to within 20 mm of the bottom of the plate at which point the channels were flared outward to form a two dimensional funnel. Plates were spotted near the apex of the funnel so that in the development of the plates all spotted material would move into the narrow channel.

All TLC plates were developed in a glass-covered developing tank which contained 100 mL of a 1:1 mixture of hexane and toluene. Plates remained in the tank until the solvent front had moved 16 cm up the plate. The plates were removed from the tank, air-dried for five minutes, and viewed in a dark cabinet under long wavelength (366 nm) and short wavelength (254 nm) UV radiation. The length of the developed band, using both wavelengths, was marked while in the viewing cabinet and the R_f value was determined from the middle of the band.

Selectivity of the alumina and silica gel plates was determined by spotting the plates with interference compounds (ST INTF 1 and ST INTF 2) and PAHs to determine if any interference occur for PAHs and whether or not band length was proportional to concentration. Sensitivity was determined by spotting the plates with various amounts of equimolar mixtures of PAHs as well as individual PAHs at different concentration levels.

VALIDATION OF SCREENING METHOD FOR PAHS

Based on the results presented in Section 6 of the experiments described above, a screening method based on solvent extraction, alumina cleanup, and measurement of total UV absorbance was selected. This method is presented in Appendix B. This method was validated by comparing the analytical results obtained for relevant water samples using the screening method to the results obtained using U.S. EPA Method 610. The method detection limit for the screening method was determined using the U.S. EPA protocol presented in Appendix A. The results of these experiments are reported in Section 6.

Sampling

Wastewater samples collected were (1) Columbus, Ohio, POTW outfall; (2) final effluent from a coking operation; and, (3) final effluent from an oil refinery. The POTW sample was collected in one-gallon glass bottles. The two industrial wastewater samples were collected in 55-gallon stainless steel drums, and transferred to one-gallon glass bottles upon arrival in the laboratory. All wastewater samples were stored at 4°C at pH 6-8 prior to extraction.

Sample Preparation

The samples were extracted and concentrated exactly as described in Appendix B. All sample extracts were subjected to alumina cleanup, even though the cleanup step is presented as an option in the method. Samples were spiked at the appropriate level using a methylene chloride solution containing equimolar concentrations of all 16 priority pollutant PAHs.

Total UV Absorbance Determination

The sample extract, in methylene chloride, was analyzed as described in Appendix B. The total PAH concentration was determined by comparing the absorbance of the sample extract to the absorbance versus concentration curve for fluoranthene. The fluoranthene calibration curve was obtained by analyzing standards having fluoranthene concentrations between 1 and 30 µg/mL. A mixture of 16 PAHs, representing 100% recovery, was also analyzed by the UV step in order to determine absolute recovery of total PAH.

HPLC Determination (U.S. EPA Method 610)

The sample extract was exchanged into acetonitrile (final volume of one milliliter) following UV analysis. The concentration of individual priority pollutant PAHs was determined using the HPLC conditions specified in U.S. EPA Method 610.

A summary of the HPLC conditions employed is given below:

Instrument:	Altex 100A gradient system
Column:	Perkin-Elmer PAH/10, 250 mm x 2.6 mm I.D.
Mobile Phase:	40/60 acetonitrile/water for five minutes, then linear gradient to 100% acetonitrile over 25 minutes, hold at 100% acetonitrile for 10 minutes
Flow Rate:	0.5 mL/minute
Fluorescence Detector:	Schoeffel FS970, excitation at 280 nm, emission 389 cutoff filter (Corning 3-75).

The instrument was calibrated using acetone standards containing all 16 PAHs at appropriate concentrations. Naphthalene, acenaphthylene, fluorene, and acenaphthene were quantified by UV detection and the remaining PAHs were quantified by fluorescence detection.

GC/MS Analysis

One extract of each wastewater (unspiked) was analyzed by GC/MS in order to confirm component identifies. The following instrument conditions were employed:

Instrument:	Finnigan 4000 with INCOS data system
Ionization Mode:	70 eV, electron impact
Scan Rate:	2 seconds/scan
Gas Chromatographic Parameters:	
Oven Temperature:	80-270°C at 4°C/minute
Column:	30 meters J and W, DB-5 fused silica
Flow Rate:	20 cm/second, helium
Injection Volume:	2 µL, splitless.

Statistical Comparison of Screening and U.S. EPA Method 610 Results

The U.S. EPA Method 610 and screening method results for each water type were subjected to linear regression analysis. The slope, intercept, correlation coefficient, and R-squared values were calculated for each water type. These data are presented in Section 6.

SECTION 6

RESULTS AND DISCUSSION

EVALUATION OF FLUORESCENCE DETECTION

In order to assess the variability in fluorescence response between the various PAHs, fluorescence intensity measurements were made using excitation wavelengths of 220, 240, 260, and 280 nm. For this experiment, a 290 nm cutoff filter (allowing radiation having a wavelength of 290 nm or greater to be detected) was used in the emission beam, with the emission grating set at zero order. These excitation wavelengths were chosen since all 16 priority pollutant PAHs have strong absorptivity in this wavelength region. An excitation slit width of 20 nm was used to achieve somewhat of an averaging effect over the wavelength region of interest. The data obtained in this experiment are shown in Table 2.

The data shown in Table 2 indicate a wide variation in fluorescence response for the 16 PAHs, even when a cutoff filter is used in the emission beam. At all four wavelengths, the ratio in fluorescence intensity between the most responsive and least responsive PAH is approximately two orders of magnitude. This ratio would become much larger if a single emission wavelength were chosen, since the use of the emission cutoff filter allows the emission to be integrated over a wide range of wavelengths.

Another feature of the fluorescence response of PAHs which was investigated was the variation in response over a range of concentration (i.e., linearity of response). The response for various concentrations of anthracene is shown in Table 3. Similar data are given for benzo(a)pyrene (using a 350 nm emission cutoff filter) in Table 4. The data in Tables 3 and 4 indicate that non-linearity in the fluorescence response for individual compounds, using these experimental conditions, is a serious problem.

In order to determine whether or not the non-linear response was a result of the broad band emission measurement, the response for benzo(a)pyrene was determined at various concentrations using an emission setting of 402 nm (grating monochrometer) and an emission slit width of 10 nm. The data obtained from this experiment are presented in Table 5. Comparison of the data in Tables 4 and 5 indicate that the non-linearity in response is less severe for benzo(a)pyrene when a single emission wavelength, rather than a broad emission band, is chosen.

In order to determine whether or not the non-linearity observed was instrument related, the response for quinine sulfate, a frequently used fluorescence reference material, was determined at various concentrations

TABLE 2. TOTAL FLUORESCENCE EMISSION
DATA FOR PAHs

PAH Compounds	Total Integrated Intensity, Arbitrary Units			
	Excitation Wavelength, nm			
	220	240	260	280
Acenaphthene	536	160	192	407
Acenaphthylene	45	20	19	28
Fluorene	399	603	1140	645
Naphthalene	112	34	69	70
Anthracene	1009	1342*	930	81
Benzo(a)anthracene	663	873	1088	1051
Benzo(b)fluoranthene	1343*	1354*	1357*	1363*
Benzo(k)fluoranthene	1358*	1367*	1364*	1372*
Benzo(ghi)perylene	357	388	538	687
Benzo(a)pyrene	1057	1332*	1343*	1347*
Chrysene	326	455	573	442
Dibenzo(a,h)anthracene	457	390	608	869
Fluoranthene	1334*	1341*	1338*	1346*
Indeno(1,2,3-cd)pyrene	1168	1335*	1334*	1338*
Phenanthrene	135	303	266	180
Pyrene	187	278	274	140
Cyclohexane (blank)	18	19	19	18

Conditions: Fluorometer - Perkin-Elmer Model MPF-44B
Excitation Slit Width - 20 nm
Emission Slit Width - 10 nm
Emission Filter - 290 nm
Integration Time - 20 s
Signal Gain - 0.1
PAH Standard Solutions - 10^{-5}M in cyclohexane + 1% $MeCl_2$.

* These fluorescence data are out of range. Signal gain cannot be reduced further.

TABLE 3. TOTAL FLUORESCENCE MEASUREMENT OF ANTHRACENE

Anthracene Concentration M	Relative Concentration	Integrated Fluorescence Intensity of Given Excitation Wavelength, Arbitrary Units — Excitation Wavelength, nm: 220	240	260	280
10^{-7}	1000	1159 (11)*	4000 (29)	2537 (17)	1302 (10)
10^{-8}	100	355 (3.2)	610 (4.4)	515 (3.6)	477 (3.8)
5×10^{-9}	50	271 (2.5)	487 (3.5)	389 (2.7)	302 (2.4)
10^{-10}	1	109 (1.0)	140 (1.0)	145 (1.0)	125 (1.0)
Cyclohexane blank		18	19	19	18

Conditions: Spectrofluorometer - Perkin-Elmer Model MPF-44B
Response - 1.2
Excitation Slit - 20 nm
Emission Slit - 10 nm
Emission Filter - 290 nm
All Standard Solutions in Cyclohexane.

* Relative response (compared to 10^{-10} M concentration) given in parenthesis.

TABLE 4. TOTAL FLUORESCENCE MEASUREMENT OF BENZO(a)PYRENE USING 350 nm CUTOFF FILTER

Concentration M	Relative Concentration	Fluorescence Intensity, Arbitrary Units	
5×10^{-7}	500	4000	(100)*
1×10^{-7}	100	773	(20)
5×10^{-8}	50	458	(12)
1×10^{-8}	10	150	(3.8)
5×10^{-9}	5	76	(1.9)
1×10^{-9}	1	39	(1.0)
Cyclohexane blank		5	

Conditions: Spectrofluorometer - Perkin-Elmer
Model MPF-44B
Excitation Wavelength - 254 nm
Excitation Slit - 20 nm
Emission Slit - 10 nm
Emission Filter - 350 nm cutoff
Response - 1.2
All standard solutions in cyclohexane.

* Relative response (compared to 10^{-9} M concentration) given in parenthesis.

TABLE 5. TOTAL FLUORESCENCE MEASUREMENT OF BENZO(a)PYRENE AT EMISSION WAVELENGTH 402 nm

Concentration M	Relative Concentration	Fluorescence Intensity, Arbitrary Units
5×10^{-7}	500	4400 (220)*
1×10^{-7}	100	830 (42)
5×10^{-8}	50	480 (24)
1×10^{-8}	10	113 (5.7)
5×10^{-9}	[illegible]	58 (2.9)
1×10^{-9}	1	20 (1.0)
Cyclohexane blank		4

Conditions: Spectrofluorometer - Perkin-Elmer Model MPF-44B
Excitation Wavelength - 254 nm
Excitation Slit - 20 nm
Emission Slit - 10 nm
Response - 1.2
All Standard Solutions in Cyclohexane

* Relative response (compared to 10^{-9} M concentration) given in parenthesis.

using a 390 nm cutoff filter in the emission beam. The response was determined using various excitation and emission slit widths. The data obtained in this experiment are presented in Table 6.

In general, the linearity in response was good for quinine sulfate at concentrations of $10^{-10}\underline{M}$ or greater. Linearity of at least three orders of magnitude was achieved at the narrowest slit widths employed (2 nm for the excitation slitwidth and 1 nm for the emission slitwidth). The linear range at larger slitwidths was less because of detector saturation.

The effect of inert gas purging on linearity was explored for several PAHs. In this experiment, the PAH cyclohexane solutions were purged with oxygen free argon for five to ten minutes just prior to measurement of the fluorescence intensity. Data for the PAHs tested are given in Table 7. Comparison of these data to the data given in Table 3 indicate that a more linear fluorescence response is obtained when argon purging is employed, although the response is still non-linear.

The data in Table 7 indicate that while argon purging reduces the degree of non-linearity in response, the response variation between one PAH to another is still very large (at least a factor of 20 between the most responsive and least responsive compounds). This result illustrates a very serious limitation on the use of fluorescence as a screening method for total PAHs.

In view of the problems associated with the fluorescence based screening method for PAHs, as well as the promising results obtained using a UV based screening method, no laboratory experiments were conducted using PAH mixtures which had been previously included in the workplan. The problems of non-linear response and variability in response between compound mixtures are likely to be more severe when mixtures of PAHs are studied. A fundamental problem encountered when dealing with PAH mixtures is the overlap of emission bands for certain PAHs with absorption bands of other PAHs. This problem is illustrated in Figure 3. For example, as shown in Figure 3, the fluorescence emission band for naphthalene overlaps severely with the benzo(a)pyrene absorption band. Hence, when benzo(a)pyrene and naphthalene are both present in a sample, the radiation emitted by naphthalene will be absorbed by benzo(a)-pyrene, thus distorting the fluorescence signal. Problems of this type cannot be avoided, and become more severe as the complexity of the PAH mixture increases. Socalled "dark reactions" or non-radiative energy transfer will also distort the fluorescence signal in some complex mixtures.

It is also worth noting that HPLC/fluorescence schemes for determining PAHs, such as U.S. EPA Method 610, have two inherent features which reduce or eliminate the problems described in this report. First, the PAHs are determined as chromatographically resolved components, thus eliminating the cross-compound absorption problems. Secondly, the mobile phase is free from oxygen, thus reducing the oxygen quenching problems and increasing the linear range of the system.

TABLE 6. TOTAL FLUORESCENCE OF QUININE SULFATE

	Concentration M	Relative Concentration	Fluorescence Intensity, Arbitrary Units
(a) Excitation slit: 20 nm Emission slit: 10 nm	10^{-9}	100	8600 (61)*
	10^{-10}	10	870 (6.2)
	10^{-11}	1	141 (1.0)
	Cyclohexane blank		6
(b) Excitation slit: 5 nm Emission Slit: 5 nm	10^{-8}	1000	21600 (570)
	10^{-9}	100	2490 (65)
	10^{-10}	10	249 (6.5)
	10^{-11}	1	38 (1.0)
	Cyclohexane blank		3
(c) Excitation slit: 2 nm Emission slit: 1 nm	10^{-7}	10,000	9000 (4,500)
	10^{-8}	1000	1020 (510)
	10^{-9}	100	91 (45)
	10^{-10}	10	10 (5.0)
	10^{-11}	1	2 (1.0)
	Cyclohexane blank		<1

Conditions: Spectrofluorometer - Perkin-Elmer Model MPF-44B
Excitation Wavelength - 350 nm
Emission Filter - 390 nm cutoff
Response - 1.2
All Standard Solutions in 0.1 $\underline{N}$ H_2SO_4.

* Relative response (compared to 10^{-11} $\underline{M}$ concentration) given in parenthesis.

TABLE 7. TOTAL FLUORESCENCE MEASUREMENTS OF ARGON PURGED PAH STANDARD SOLUTIONS

PAH Solution	Concentration M	Relative Concentrations	Fluorescence Intensity, Arbitrary Units λex 340 nm	λex 255 nm
Anthracene	10^{-5}	1000	20700 (330)*	13700 (190)*
	10^{-6}	100	4200 (68)	4200 (59)
	10^{-7}	10	1070 (17)	1170 (16)
	10^{-8}	1	62 (1.0)	71 (1.0)
Benzo(b)fluoranthene	10^{-5}	1000	37000 (410)	42500 (530)
	10^{-6}	100	3300 (37)	6300 (79)
	10^{-7}	10	900 (10)	1130 (14)
	10^{-8}	1	90 (1.0)	80 (1.0)
Chrysene	10^{-5}	1000	3300 (330)	4200 (210)
	10^{-6}	100	400 (40)	1270 (64)
	10^{-7}	10	63 (6.3)	187 (9.4)
	10^{-8}	1	10 (1.0)	20 (1.0)
Fluoranthene	10^{-5}	1000	19700 (428)	16300 (708)
	10^{-6}	100	2270 (50)	1330 (58)
	10^{-7}	10	350 (7.6)	233 (10)
	10^{-8}	1	46 (1.0)	23 (1.0)
Indeno(1,2,3-cd)pyrene	10^{-5}	1000	17300	16700 (670)
	10^{-6}	100	3330	2870 (115)
	10^{-7}	10	283	250 (10)
	10^{-8}	1	31	25 (1.0)
Phenanthrene	10^{-5}	1000	1730	1900 (480)
	10^{-6}	100	280	300 (75)
	10^{-7}	10	41	43 (11)
	10^{-8}	1	4	4 (1.0)
Cyclohexane blank			<1	<1

Conditions: Spectrofluorometer - Perkin-Elmer Model MPF-44B
Response - 1.2
Excitation Slit - 10 nm
Emission Slit - 1 nm
Emission Filter - 350 nm cutoff

* Relative response (compared to 10^{-8} M concentration) given in parenthesis.

Based on the information presented above, the use of fluorescence as a screening method for PAHs does not appear to be practical. While the problem of non-linear response can be reduced substantially by inert gas purging, the compound to compound variability in response and intercompound absorption problems are inherent in the method, and severely restrict its usefulness.

EVALUATION OF UV DETECTION

The determination of total PAH concentration by monitoring UV absorbance was accomplished using two approaches. The first approach (the multiple wavelength method) involves monitoring the absorbance at two or more specified wavelengths and performing a weighted average calculation to determine total PAH concentration. This approach is useful only if two wavelengths are found such that each of the components of interest absorb strongly at one of the wavelengths but not at both wavelengths. This approach becomes difficult as the number of components of interest increases.

The second approach, called the total UV measurement approach, involves making a single UV absorbance measurement over a wide wavelength region, over which the average molar absorptivities of the components of interest are approximately equal.

In order to evaluate which of these UV methods would be most appropriate for the PAHs, the molar absorptivity of the PAHs over specified wavelength regions were calculated from literature data (30). These data are presented in Tables 8 and 9. As shown in Table 8, the average molar absorptivities of the PAHs over narrow (10 nm) wavelength regions vary over two orders of magnitude. The data given in Table 9 indicate that molar absorptivities over certain wavelength regions (e.g., 240-320) vary by a factor of 15. Since the most responsive components are the high molecular weight components (e.g., dibenzo(a,h)anthracene), the variation in response on a weight basis is substantially less.

In view of the high variation in response for PAHs over narrow wavelength ranges, and the greater complexity of the multiple wavelength approach, the total UV approach was selected for laboratory evaluation.

Two optical filters were evaluated for use in the total UV measurement. The transmission curves for these filters are presented in Figures 1 and 2. The first filter, Corning 7-54, is a bandpass filter transmitting UV radiation in the 240-380 nm region whereas the second filter, Corning 9-54 is a cutoff filter transmitting UV radiation above 230 nm.

The apparent molar absorptivities and relative response (on a weight basis) for various PAHs using these two filters are presented in Tables 10 and 11. Examination of the data in Tables 10 and 11 reveals that a smaller compound to compound variation in response is obtained using the bandpass filter than using the cutoff filter. Sensitivity for the various compounds was somewhat better using the bandpass filter (except in the case of naphthalene which gave a slightly higher response using the cutoff filter).

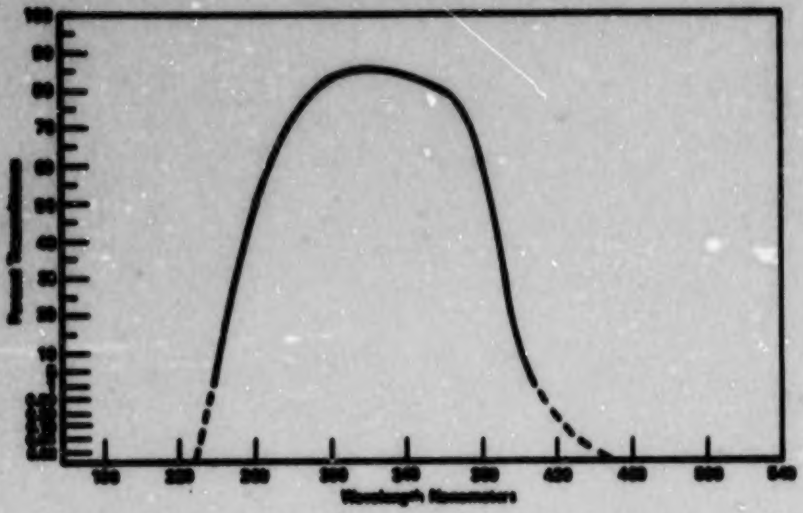


Figure 1. Transmittance curve for Corning bandpass filter type 7-54.

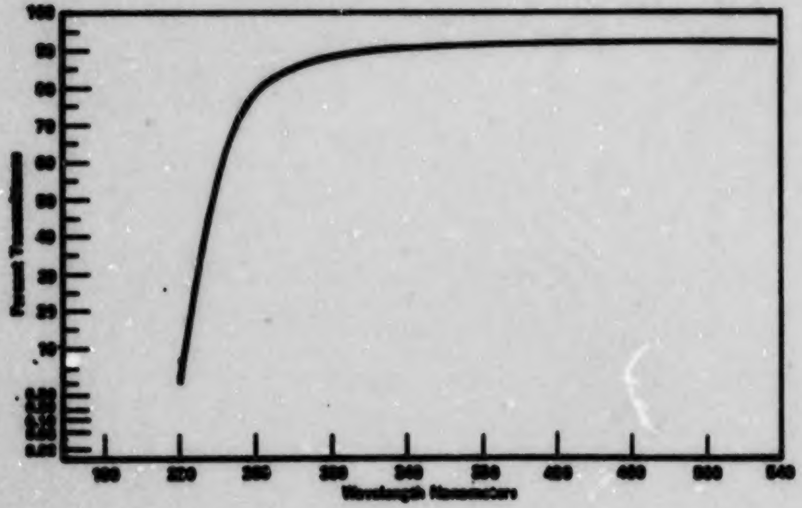


Figure 2. Transmittance curve for Corning cutoff fitler type 9-54.

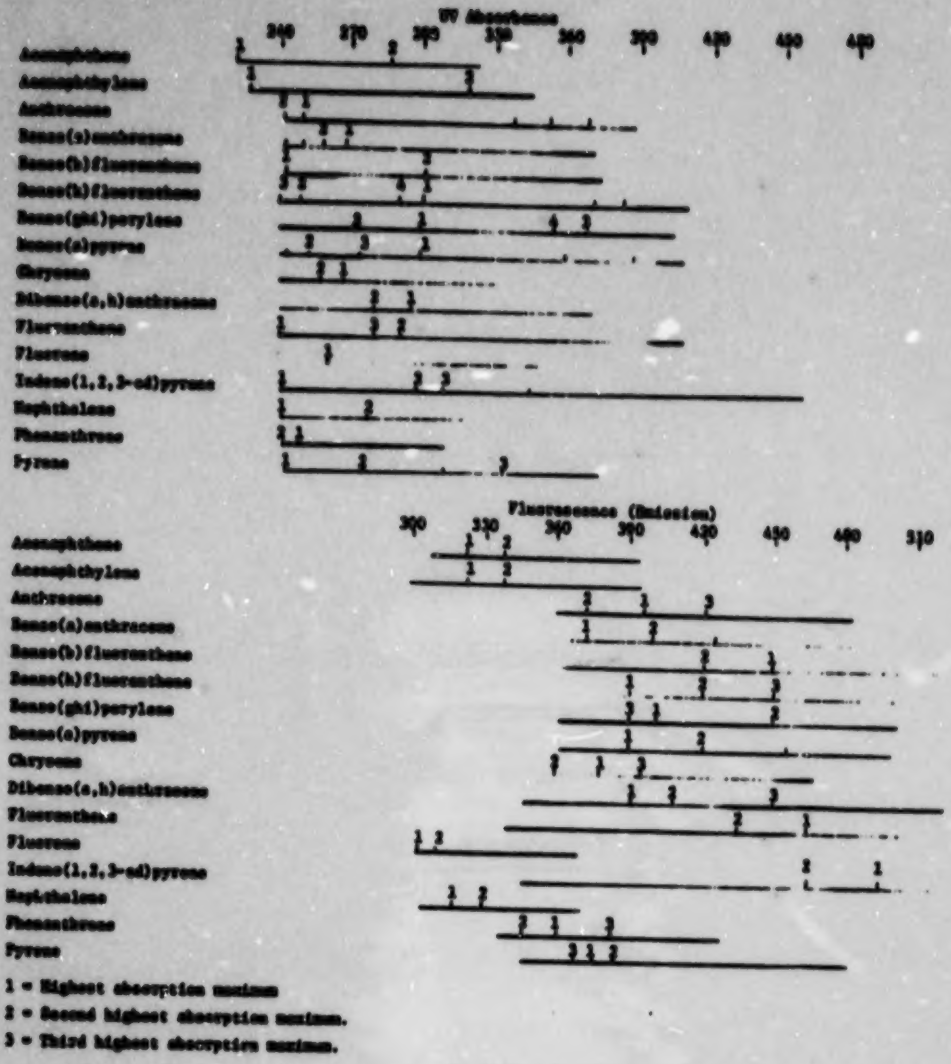


Figure 3. Compilation of UV absorbance and fluorescence emission data for priority pollutant PAHs.

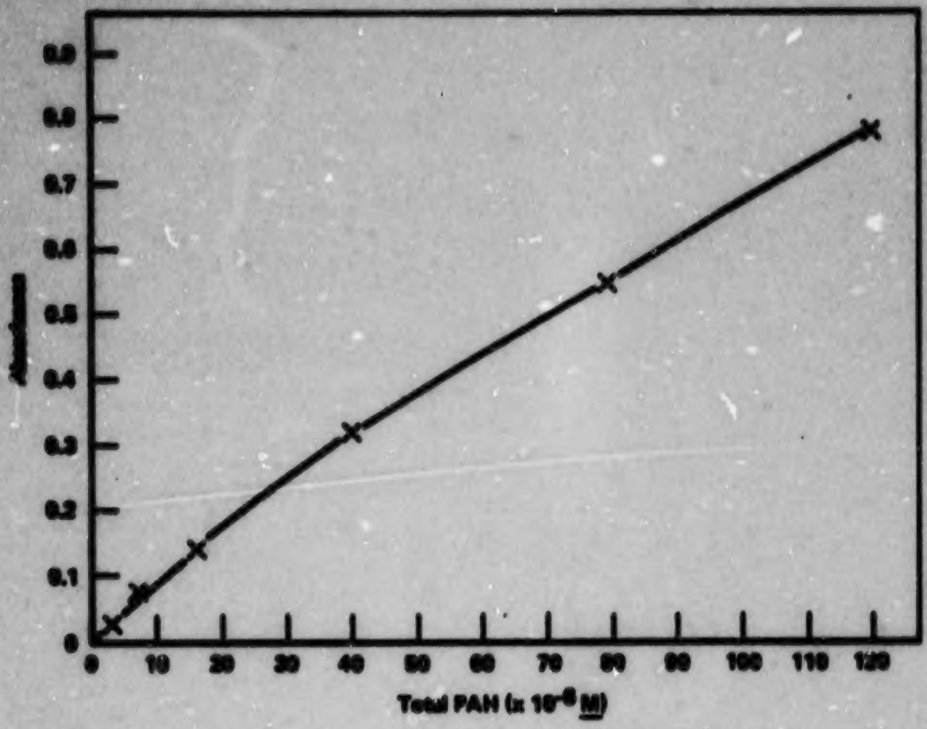


Figure 4. Calibration curve for equimolar mixture of 16 priority pollutant PAHs using total UV method.

TABLE 8. ANALYSIS OF ULTRAVIOLET SPECTRA FOR POLYCYCLIC AROMATIC HYDROCARBONS — MULTIPLE WAVELENGTH METHOD

#	Compound	240-250 nm $\bar{\epsilon}$	a_r	250-260 nm $\bar{\epsilon}$	a_r	260-270 nm $\bar{\epsilon}$	a_r	270-280 nm $\bar{\epsilon}$	a_r
1.	Acenaphthene	1410	1.0	1880	1.1	3260	2.4	5370	15
2.	Acenaphthylene	1480	1.0	1620	1.0	2880	1.3	1510	4.2
3.	Anthracene	77000	55	65500	39	1230	1.0	380	1.0
4.	Benzo(a)anthracene	18600	13	30900	19	38000	20	40000	126
5.	Benzo(e)pyrene	21900	16	36300	22	40700	30	25900	82
6.	Benzo(ghi)perylene	13500	9.6	18300	11	20900	15	24000	67
7.	Benzo(k)fluoranthene	53700	38	24500	15	17000	13	16200	45
8.	Chrysene	22400	16	53700	33	93300	69	23600	65
9.	Dibenzo(a,h)anthracene	8510	6.0	12600	7.8	25100	19	46000	139
10.	Fluoranthene	16400	12	12000	7.4	10500	7.8	15100	42
11.	Fluorene	10200	7.2	17000	11	18000	13	11200	31
12.	Naphthalene	1700	1.2	2950	1.8	4470	3.3	4800	14
13.	Phenanthrene	44700	32	42700	26	16600	12	12600	35
14.	Pyrene	22400	16	13200	8.1	22600	17	15100	42

#	Compound	280-290 nm $\bar{\epsilon}$	a_r	290-300 nm $\bar{\epsilon}$	a_r	300-310 nm $\bar{\epsilon}$	a_r	310-320 nm $\bar{\epsilon}$	a_r
1.	Acenaphthene	6170	26	5370	15	2950	16	1150	19
2.	Acenaphthylene	1580	6.6	3310	8.9	5370	28	7580	125
3.	Anthracene	240	1.0	370	1.0	740	3.9	1260	21
4.	Benzo(a)anthracene	51300	214	13200	36	5500	29	5130	85
5.	Benzo(e)pyrene	36300	151	36300	98	5750	30	2950	49
6.	Benzo(ghi)perylene	27500	115	34700	94	33000	178	6760	113
7.	Benzo(k)fluoranthene	22400	93	38000	103	47900	252	14000	367
8.	Chrysene	11500	48	11200	30	11000	58	9500	159
9.	Dibenzo(a,h)anthracene	60300	251	72400	196	49000	258	17000	283
10.	Fluoranthene	17800	74	2510	6.8	3030	16	3900	65
11.	Fluorene	4900	20	5250	14	1550	8.2	750	12
12.	Naphthalene	3310	14	500	1.4	190	1.0	60	1.0
13.	Phenanthrene	7590	32	3800	10	250	1.3	360	2.7
14.	Pyrene	2950	12	4600	13	8910	47	17000	283

TABLE 8. (Continued)

#	Compound	320-330 nm		330-340 nm		340-350 nm		350-360 nm		360-370 nm	
		$\bar{\varepsilon}$	a_r	$\bar{\varepsilon}$	a_r	$\bar{\varepsilon}$	a_r	$\bar{\varepsilon}$	a_r	$\bar{\varepsilon}$	a_r
1.	Acenaphthene	400	8.0	0	—	0	—	0	—	0	—
2.	Acenaphthylene	8320	166	3720	74	1800	36	600	12	400	10
3.	Anthracene	2190	44	3470	69	3160	63	5370	107	2160	54
4.	Benzo(a)anthracene	5620	112	5130	103	4900	98	3720	74	1550	39
5.	Benzo(a)pyrene	3390	68	5750	115	9550	191	13300	266	19500	488
6.	Benzo(ghi)perylene	4170	83	4570	91	7410	148	8500	170	18600	465
7.	Benzo(k)fluoranthene	6920	138	5250	105	3890	78	4270	85	5010	125
8.	Chrysene	4570	91	710	14	490	9.8	340	6.8	230	5.8
9.	Dibenzo(a,h)anthracene	16200	324	13200	264	7940	159	4800	96	680	17
10.	Fluoranthene	5010	100	5620	112	7080	142	7080	142	4000	100
11.	Fluorene	750	15	750	15	750	15	750	15	500	12
12.	Naphthalene	50	1.0	50	1.0	50	1.0	50	1.0	40	1.0
13.	Phenanthrene	190	3.8	170	3.4	90	1.8	0	—	0	—
14.	Pyrene	15800	316	19500	390	1260	25	390	7.8	210	5.2

#	Compound	370-380 nm		380-390 nm		390-400 nm		400-410 nm		410-420 nm	
		$\bar{\varepsilon}$	a_r	$\bar{\varepsilon}$	a_r	$\bar{\varepsilon}$	a_r	$\bar{\varepsilon}$	a_r	$\bar{\varepsilon}$	a_r
1.	Acenaphthene	0	—	0	—	0	—	0	—	0	—
2.	Acenaphthylene	250	8.3	250	8.3	250	12	200	1.0	200	1.0
3.	Anthracene	4000	133	600	20	300	15	0	—	0	—
4.	Benzo(a)anthracene	500	17	500	17	0	—	0	—	0	—
5.	Benzo(a)pyrene	16600	553	17400	580	1910	96	1860	9.3	250	1.2
6.	Benzo(ghi)perylene	10500	350	21400	713	2090	104	250	1.2	0	—
7.	Benzo(k)fluoranthene	7940	265	6920	231	7590	380	7700	38	870	4.4
8.	Chrysene	200	6.7	200	6.7	40	2.0	0	—	0	—
9.	Dibenzo(a,h)anthracene	550	18	340	11	380	19	0	—	0	—
10.	Fluoranthene	1200	40	400	13	100	5.0	0	—	0	—
11.	Fluorene	500	17	500	17	500	25	200	1.0	0	—
12.	Naphthalene	30	1.0	30	1.0	20	1.0	0	—	0	—
13.	Phenanthrene	0	—	0	—	0	—	0	—	0	—
14.	Pyrene	100	3.3	0	—	0	—	0	—	0	—

$\bar{\varepsilon}$ = Average molar absorptivity over the specified range

a_r = Average molar absorptivity relative to the least responsive compound in the specified range

TABLE 9. ANALYSIS OF ULTRAVIOLET SPECTRA FOR POLYCYCLIC AROMATIC HYDROCARBONS — TOTAL UV ABSORBANCE METHOD.

#	Compound	240–250 nm		240–260 nm		240–270 nm		240–280 nm		240–290 nm	
		$\bar{\epsilon}$	σ_r	$\bar{\epsilon}$	σ_r	$\bar{\epsilon}$	σ_r	$\bar{\epsilon}$	σ_r	$\bar{\epsilon}$	σ_r
1.	Acenaphthene	1410	1.0	3270	1.1	6510	1.3	11900	1.6	18000	2.2
2.	Acenaphthylene	1480	1.0	3100	1.0	5100	1.0	6610	1.9	8150	1.8
3.	Anthracene	77600	55	141000	45	142000	20	143000	21	163000	17
4.	Benzo(a)anthracene	18600	13	49500	16	87300	17	126000	21	188000	23
5.	Benzo(a)pyrene	21900	16	56200	19	98000	19	128000	19	162000	20
6.	Benzo(ghi)perylene	13500	9.6	31700	10	52000	18	76600	12	104000	13
7.	Benzo(k)fluoranthene	53700	38	78200	25	96000	19	112000	17	125000	16
8.	Chrysene	22400	16	76100	25	160000	33	193000	29	204000	25
9.	Dibenzo(a,h)anthracene	8510	6.0	21100	6.8	46300	9.1	93800	14	153000	19
10.	Fluoranthene	16600	12	28000	9.2	39100	7.7	56200	8.2	73000	8.8
11.	Fluorene	10200	7.2	28000	9.0	46200	9.1	57600	8.7	62200	7.6
12.	Naphthalene	1700	1.2	4650	1.5	9120	1.8	16000	2.1	17300	2.1
13.	Phenanthrene	44700	32	87600	28	104000	20	117000	18	124000	15
14.	Pyrene	22400	16	35600	11	58000	11	73600	11	76000	9.3

#	Compound	240–300 nm		240–310 nm		240–320 nm		240–330 nm		240–340 nm		240–350 nm	
		$\bar{\epsilon}$	σ_r	$\bar{\epsilon}$	σ_r	$\bar{\epsilon}$	σ_r	$\bar{\epsilon}$	σ_r	$\bar{\epsilon}$	σ_r	$\bar{\epsilon}$	σ_r
1.	Acenaphthene	23600	2.0	26400	1.6	27300	1.5	27900	1.5	27900	1.5	27900	1.5
2.	Acenaphthylene	11500	1.0	16900	1.0	24500	1.4	32000	1.8	36500	2.0	38300	2.1
3.	Anthracene	143000	12	144000	8.5	145000	8.0	147000	8.1	153000	8.3	156000	8.5
4.	Benzo(a)anthracene	201000	17	206000	12	212000	12	217000	12	223000	12	227000	12
5.	Benzo(a)pyrene	201000	17	207000	12	210000	12	213000	12	219000	12	220000	13
6.	Benzo(ghi)perylene	139000	12	173000	10	179000	9.9	184000	10	188000	10	190000	11
7.	Benzo(k)fluoranthene	173000	15	220000	13	235000	13	242000	13	247000	14	250000	14
8.	Chrysene	216000	19	226000	13	236000	13	241000	13	241000	13	242000	13
9.	Dibenzo(a,h)anthracene	226000	20	275000	16	292000	16	300000	17	321000	18	330000	18
10.	Fluoranthene	74500	6.5	77300	4.6	81400	4.5	86400	4.8	92000	5.1	98100	5.4
11.	Fluorene	67600	5.9	69100	4.1	69000	3.9	70600	3.9	71300	3.9	72100	4.0
12.	Naphthalene	17800	1.5	18000	1.1	18100	1.0	18100	1.0	18200	1.0	18200	1.0
13.	Phenanthrene	128000	11	129000	7.6	129000	7.1	129000	7.1	129000	7.1	129000	7.1
14.	Pyrene	80700	7.0	89600	5.3	107000	5.9	122000	6.7	142000	7.8	143000	7.9

TABLE 9. (Continued)

#	Compound	240-360 nm $\bar{\varepsilon}$	σ_ε	240-370 nm $\bar{\varepsilon}$	σ_ε	240-380 nm $\bar{\varepsilon}$	σ_ε	240-390 nm $\bar{\varepsilon}$	σ_ε	240-400 nm $\bar{\varepsilon}$	σ_ε	240-410 nm $\bar{\varepsilon}$	σ_ε
1.	Acenaphthene	27900	1.5	27900	1.5	27900	1.5	27900	1.5	27900	1.5	27900	1.5
2.	Acenaphthylene	38900	2.1	39300	2.1	39600	2.2	39800	2.2	40000	2.2	40200	2.2
3.	Anthracene	159000	8.7	161000	8.8	163000	9.0	164000	9.0	166000	9.0	166000	9.0
4.	Benzo(a)anthracene	231000	13	232000	13	233000	13	234000	13	234000	13	234000	13
5.	Benzo(a)pyrene	241000	13	260000	14	277000	15	284000	16	290000	16	290000	16
6.	Benzo(ghi)perylene	204000	11	223000	12	233000	13	255000	14	257000	14	257000	14
7.	Benzo(k)fluoranthene	256000	14	261000	14	269000	15	278000	15	283000	15	291000	16
8.	Chrysene	243000	13	243000	13	243000	13	243000	13	243000	13	243000	13
9.	Dibenzo(a,h)anthracene	334000	18	335000	18	335000	18	336000	18	336000	18	336000	18
10.	Fluoranthene	106000	5.8	110000	6.0	111000	6.0	112000	6.1	112000	6.1	112000	6.1
11.	Fluorene	73000	4.0	73400	4.0	73000	4.0	74400	4.0	74800	4.1	75000	4.1
12.	Naphthalene	18300	1.0	18300	1.0	18400	1.0	18400	1.0	18400	1.0	18400	1.0
13.	Phenanthrene	129000	7.0	129000	7.0	129000	7.0	129000	7.0	129000	7.0	129000	7.0
14.	Pyrene	144000	7.9	144000	7.9	144000	7.8	144000	7.8	144000	7.8	144000	7.8

#	Compound	240-420 nm $\bar{\varepsilon}$	σ_ε	240-430 nm $\bar{\varepsilon}$	σ_ε	230-370 nm $\bar{\varepsilon}$	σ_ε	230-380 nm $\bar{\varepsilon}$	σ_ε	230-390 nm $\bar{\varepsilon}$	σ_ε	230-400 nm $\bar{\varepsilon}$	σ_ε
1.	Acenaphthene	27500	1.5	27900	1.5	26300	1.6	26300	1.6	26500	1.6	26500	1.6
2.	Acenaphthylene	40400	2.2	40400	2.2	37000	2.3	38100	2.3	38300	2.3	38500	2.3
3.	Anthracene	166000	9.0	166000	9.0	83400	5.0	87400	5.2	88400	5.3	88900	5.3
4.	Benzo(a)anthracene	234000	13	234000	13	214000	13	214000	13	213000	13	213000	13
5.	Benzo(a)pyrene	290000	16	290000	16	230000	14	255000	15	273000	16	276000	16
6.	Benzo(ghi)perylene	257000	14	257000	14	210000	13	220000	13	263000	14	264000	15
7.	Benzo(k)fluoranthene	292000	16	292000	16	207000	12	213000	13	222000	13	229000	14
8.	Chrysene	243000	13	243000	13	220000	13	222000	13	222000	13	221000	13
9.	Dibenzo(a,h)anthracene	336000	18	336000	18	326000	20	326000	20	327000	20	327000	20
10.	Fluoranthene	112000	6.1	112000	6.1	93400	5.6	94400	5.7	95400	5.7	95400	5.7
11.	Fluorene	75000	4.1	75000	4.1	63200	3.8	63600	3.8	64200	3.8	64600	3.9
12.	Naphthalene	18400	1.0	18400	1.0	16400	1.0	16700	1.0	16700	1.0	16700	1.0
13.	Phenanthrene	129000	7.0	129000	7.0	84300	5.1	84300	5.0	84300	5.0	84300	5.0
14.	Pyrene	144000	7.8	144000	7.8	122000	7.3	122000	7.3	122000	7.3	122000	7.3

TABLE 9. (Continued)

#	Compound	250-410 nm $\bar{\varepsilon}$	 a_r	260-370 nm $\bar{\varepsilon}$	 a_r	260-380 nm $\bar{\varepsilon}$	 a_r	260-390 nm $\bar{\varepsilon}$	 a_r	260-400 nm $\bar{\varepsilon}$	 a_r	260-410 nm $\bar{\varepsilon}$	 a_r
1.	Acenaphthene	26500	1.6	24600	1.8	24600	1.8	24600	1.8	24600	1.8	24600	1.8
2.	Acenaphthylene	38700	2.3	36200	2.7	36500	2.6	36700	2.7	36900	2.7	37100	2.7
3.	Anthracene	88400	5.3	20300	1.5	24300	1.8	25300	1.8	25300	1.8	25300	1.8
4.	Benzo(a)anthracene	215000	13	184000	14	184000	13	184000	13	184000	13	184000	13
5.	Benzo(a)pyrene	276000	17	202000	15	219000	16	236000	17	[illegible]	17	240000	17
6.	Benzo(ghi)perylene	244000	15	191000	14	201000	15	223000	16	225000	16	225000	16
7.	Benzo(k)fluoranthene	237000	14	183000	13	191000	14	198000	14	205000	15	213000	15
8.	Chrysene	221000	13	166000	12	167000	12	167000	12	167000	12	167000	12
9.	Dibenzo(a,h)anthracene	327000	20	314000	23	314000	23	315000	23	315000	23	315000	23
10.	Fluoranthene	95400	5.7	81400	6.0	82400	6.0	83400	6.0	83400	6.0	83400	6.0
11.	Fluorene	64800	3.9	45400	3.3	45800	3.3	46400	3.4	46800	3.4	47000	3.4
12.	Naphthalene	16700	1.0	13600	1.0	13800	1.0	13800	1.0	13800	1.0	13900	1.0
13.	Phenanthrene	84300	5.0	41600	3.1	41600	3.0	41600	3.0	41600	3.0	41600	3.0
14.	Pyrene	122600	7.3	108000	7.9	108000	7.8	108000	7.8	108000	7.8	108000	7.8

$\bar{\varepsilon}$ = Average molar absorptivity over the specified range
a_r= Average molar absorptivity relative to the least responsive compound in the specified range

TABLE 10. TOTAL UV ABSORPTIVITY USING BANDPASS FILTER

Compound	Apparent Molar[(a)] Absorptivity $\bar{\varepsilon}$	Absorptivity[(b)] Ratio a_r	MW	Det. Limit A = 0.01 (μg/L)	Relative[(c)] Sensitivity a_r
Naphthalene	1200	1.0	128	1000	1.0
Acenaphthene	1900	1.6	152	800	1.3
Acenaphthylene	3500	2.9	154	400	2.4
Fluorene	3200	2.7	166	500	2.1
Anthracene	4300	3.6	178	400	2.6
Phenanthrene	4700	3.9	178	400	2.8
Pyrene	7800	6.5	202	300	4.1
Fluoranthene	7500	6.2	202	300	4.0
Benzo(a)anthracene	10600	8.8	228	200	5.0
Chrysene	7200	6.0	228	300	3.4
Benzo(a)pyrene	13100	11	252	200	5.5
Benzo(b)fluoranthene	11400	9.5	252	200	4.8
Benzo(k)fluoranthene	11900	9.9	252	200	5.0
Dibenzo(a,h)anthracene	16000	13	278	200	6.1
Benzo(ghi)perylene	11300	9.4	276	200	4.4
Indeno(1,2,3-c,d)pyrene	14300	12	276	200	5.5

Conditions: UV Spectrophotometer - Perkin-Elmer Model 55B
Filter - Corning CS #7-54 Bandpass Filter
Concentration of PAH Standard Solutions - 10^{-5} M
Solvent - 1% Methylene Chloride in Cyclohexane
Light Path Length - 10 mm

(a) Apparent Molar Absorptivity $\bar{\varepsilon}$ = A/bc
A = absorbance; b = light path length, cm; c = concentration, mole/L

(b) Absorptivity Ratio a_r = molar absorptivity of PAH compound relative to molar absorptivity of naphthalene

(c) Relative Sensitivity S_r = (MW for naphthalene/MW for PAH compound) x a_r

TABLE 11. TOTAL UV ABSORPTIVITY USING CUTOFF FILTER

Compound	Apparent Molar[a] Absorptivity $\bar{\varepsilon}$	Absorptivity[b] Ratio a_r	MW	Det. Limit A = 0.01 (ug/L)	Relative[c] Sensitivity s_r
Naphthalene	1600	1.6	128	800	1.9
Acenaphthene	1000	1.0	152	1500	1.0
Acenaphthylene	2300	2.3	154	600	2.3
Fluorene	2400	2.4	166	700	2.2
Anthracene	3200	3.2	178	500	2.7
Phenanthrene	3100	3.1	178	500	2.6
Pyrene	6100	6.1	202	300	4.6
Fluoranthene	4700	4.7	202	400	3.5
Benzo(a)anthracene	7400	7.4	228	300	4.9
Chrysene	5500	5.5	228	400	3.7
Benzo(a)pyrene	11,400	11.4	252	200	6.9
Benzo(b)fluoranthene	7800	7.8	252	300	4.7
Benzo(k)fluoranthene	8400	8.4	252	300	5.1
Dibenzo(a,h)anthracene	8200	8.2	278	300	4.5
Benzo(ghi)perylene	9200	9.2	276	300	5.1
Indeno(1,2,3-cd)pyrene	12,900	12.9	276	200	7.1

Conditions: UV Spectrophotometer - Perkin-Elmer Model 55B
Filter - Corning CS 9-54 cutoff filter
Concentration of PAH Standard Solutions - 10^{-5} M
Solvent - 1% methylene chloride in cyclohexane
Light Path Length - 10 mm

(a) Apparent Molar Absorptivity $\bar{\varepsilon} = A/bc$
A = absorbance; b = light path length, cm; c = concentration, mole/L.

(b) Absorptivity Ratio a_r = molar absorptivity of PAH compound relative to molar absorptivity of acenaphthene.

(c) Relative Sensitivity s_r = (MW for acenaphthene/MW for PAH compound) x a_r.

Consequently, the bandpass filter was chosen for use in all later experiments.

The linearity in response using the total UV approach was evaluated using a solution containing equimolar concentrations of all 16 priority pollutant PAHs in cyclohexane. The plot of total PAH concentration versus absorbance is shown in Figure 4. These data indicate that the response is nearly linear over the 4-120 $\underline{\mu M}$ range or approximately 0.8-24 μg/mL (using an average molecular weight of 200 daltons).

The response data for individual PAHs as a function of concentration using the total UV approach are shown in Table 12. As indicated by the data in Table 12, the response for many of the compounds is not linear over a wide range of concentrations. It is important to recognize that the concentrations of the individual components in this experiment are approximately 20 times greater than in the previous experiment where good linearity was obtained. This result implies that the total UV determination should be conducted within a rather narrow absorbance region (∿0.05-0.35 absorbance units) so that nonlinear response does not bias the data. Dilution of sample extracts will be required to achieve this criterion in some cases.

The compound used for instrument calibration in the total UV method should have a molar absorptivity close to the average molar absorptivity of the 16 priority pollutant PAHs and should also exhibit good linearity so that a degree of bias introduced into the method can be minimized. The reference compound should also be readily available in pure form, have a low cost, and not be a carcinogen. Initially, anthracene was chosen as the reference compound for calibration purposes since it appeared to best meet these requirements. However, examination of the response data in Table 12 led to the conclusion that fluoranthene would be a better calibration standard, since it gave more nearly linear response over the desired absorbance range. Fluoranthene has the advantages that; 1) it is not a carcinogen, 2) it is readily available in pure form at low cost, and 3) its total UV response is near the median for the priority pollutant PAHs. Consequently, all further measurements using the total UV approach were made using fluoranthene as the calibration standard. The calibration curve was generally constructed over fluoranthene concentrations of 5×10^{-6} to 10^{-4} $\underline{M}$ or 1 to 20 μg/mL. Results were calculated as fluoranthene equivalents by comparing the UV absorbance for the sample extract to the fluoranthene calibration curve. A typical calibration curve for fluoranthene is shown in Figure 5.

EVALUATION OF COLUMN CLEANUP APPROACHES

Silica gel and alumina adsorbents were evaluated in terms of ability to selectively remove interfering compounds, as described in Section 5 of this report. The results obtained using these two adsorbents are described below.

TABLE 12. APPARENT MOLAR ABSORPTIVITY OF PAH AT SELECTED CONCENTRATIONS

Compound	Apparent Molar Absorptivity[(a)]						Relative Sensitivity[(b)]
Concentration, M	10^{-3}	5×10^{-4}	10^{-4}	5×10^{-5}	10^{-5}	5×10^{-6}	Sr
Naphthalene	185	—	774	1,833	1,833	—	0.47
Acenaphthylene	773	1,194	2,501	3,099	2,899	—	0.62
Acenaphthene	261	474	1,158	1,956	1,794	—	0.39
Fluorene	215	389	1,433	2,154	2,768	—	0.55
Phenanthrene	282	—	1,487	2,407	4,092	—	0.90
Anthracene	775	1,175	2,234	2,513	3,590	—	0.66
Fluoranthene	1,207	2,121	4,348	5,719	6,139	5,214	1.00
Pyrene	637	1,188	3,522	4,982	8,760	11,862	1.40
Benzo(a)anthracene	1,135	—	5,010	7,069	14,286	19,667	2.10
Chrysene	523	—	2,975	4,823	8,571	11,764	1.20
Benzo(b)fluoranthene	1,280	—	7,539	11,055	15,220	20,650	2.00
Benzo(k)fluoranthene	1,963	—	7,720	—	14,376	16,543	1.90
Benzo(a)pyrene	2,134	—	8,568	—	17,674	20,907	2.30
Dibenzo(a,h)anthracene	—	1,760	—	8,847	18,634	17,262	2.20
Benzo(ghi)perylene	—	3,403	—	11,633	17,014	15,720	2.00
Indeno(1,2,3-cd)pyrene	—	3,909	—	14,377	17,259	17,070	2.10

Conditions: UV Spectrometer - Perkin-Elmer Model 55B.
Filter - Corning CS 7-54 band-pass filter.
Solvent - Methylene chloride.
Light Path Length - 10 mm.

(a) Apparent Molar Absorptivity $\bar{E} = A/bc$
A = absorbance; b = light path length, cm; c = concentration, mole/L.

(b) Relative Sensitivity Sr = (MW fluoranthene/MW for PAH compound) x
($\bar{E}$ for PAH compound at 10^{-5}M/$\bar{E}$ for fluoranthene at 10^{-5}M)

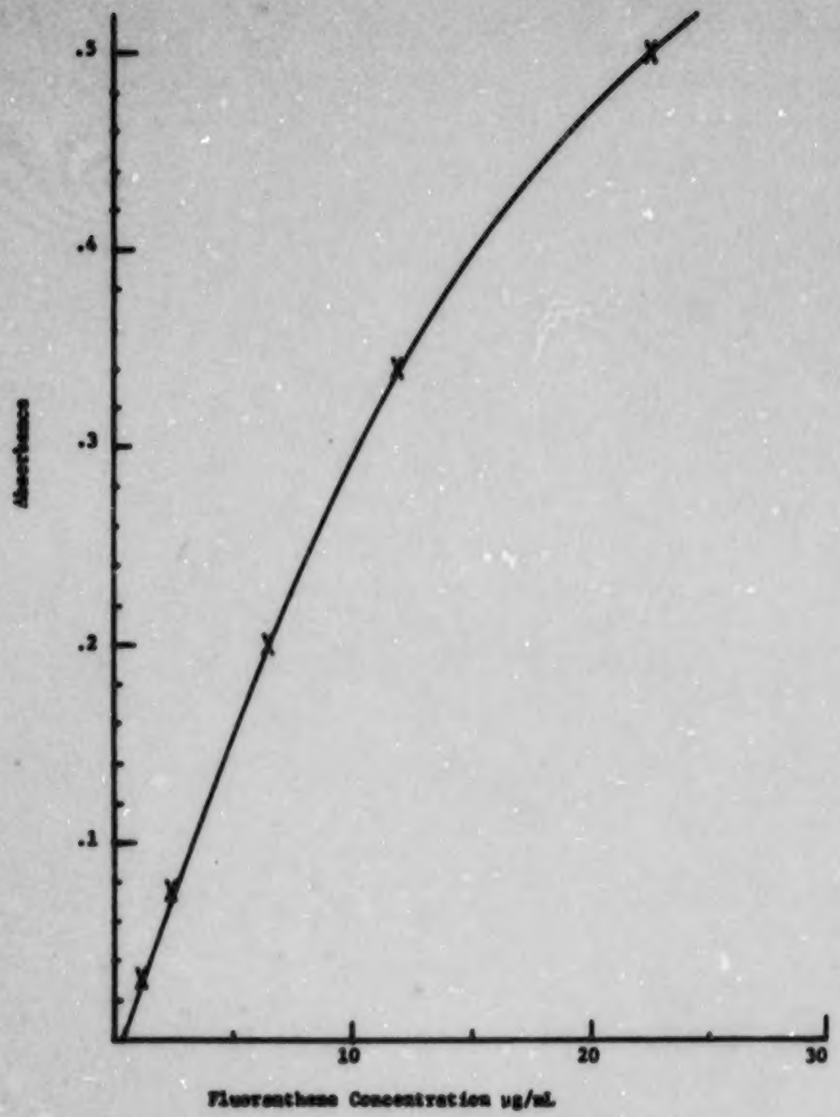


Figure 5. Fluoranthene calibration curve.

Silica Gel Column Cleanup

Silica gel columns were prepared using the procedure described in U.S. EPA Method 610. Initial experiments involved eluting the ST INTF 1 and ST INTF 2 interference solutions, and collecting and analyzing the "PAH fraction". Concentrations of ST INTF 1 and ST INTF 2 were 100 µg/mL of each compound. As described in Section 5, ST INTF 1 contains nonpolar compounds (e.g., benzene, PCBs) and ST INTF 2 contains polar components (e.g., nitrogen heterocyclics).

Because DOP is a widespread contaminant in wastewater, this compound was examined separately at a concentration level of 10^{-3} M. PAHs were analyzed at a concentration level of 10^{-5} M per compound. All samples were applied to the silica gel column at a volume of 1.0 mL.

Three chromatographic fractions were obtained for the samples listed above (applied separately) as follows:

- Fraction 1 - 25 mL of pentane
- Fraction 2 - 25 mL of 40% $MeCl_2$ in pentane
- Fraction 3 - 25 mL of $MeCl_2$.

The UV absorbance of each of these fractions at 230 nm was determined.

The UV absorbance data indicated that silica gel readily separates the polar compounds (ST INTF 2 and DOP) from the PAHs since UV absorbance was noted only in the methylene chloride fraction (Fraction 3) for these compounds. However, some of the nonpolar compounds were found to elute in the PAH fraction (Fraction 2). All of the PAHs were found to elute in Fraction 2, as expected.

Additional experiments were conducted to determine which specific nonpolar compounds were eluting in the PAH fraction and to determine the elution volumes. If these compounds were eluting near the initial elution volume where PAH fraction collection began, then by addition of a larger amount of pentane these compounds could be separated from the PAH fraction.

Elution of the ST INTF 1 solution was performed with fraction collection at 10 mL, 10 mL, and 5 mL of pentane followed by 5 mL, 10 mL, and 10 mL, or 40% $MeCl_2$ in pentane. These fractions were concentrated by Kuderna-Danish evaporation on a water bath at 50°C and analyzed by GC. Compound identification was based on retention time and recoveries were determined by comparing the peak areas obtained for the components in the fractions to the peak areas obtained for the ST INTF 1 stock solution.

Results of these analyses, listed in Table 13, indicate that trimethylbenzene and 2,4,2',4'-tetrachlorobiphenyl elute at the very end of the PAH fraction. Therefore, it is not possible to separate these compounds from PAHs using silica gel. Since PCBs absorb UV radiation and are frequently present in environmental samples, this finding represents a serious limitation of the silica gel cleanup procedure when UV absorbance is used as the determinative procedure for PAHs.

TABLE 13. ELUTION CHARACTERISTICS OF NONPOLAR COMPOUNDS ON SILICA GEL

Fraction	Compound	% Eluted
1. 10 ml pentane	no elution	
2. 10 ml pentane	hexachlorobenzene	86
3. 5 ml pentane	1,2,4-trichlorobenzene	101
	hexachlorobenzene	43
	2,4,6,2',4',6'-hexachlorobiphenyl	67
4. 5 ml 40% $MeCl_2$ in pentane	2,4,6,2',4',6'-hexachlorobiphenyl	29
5. 10 ml 40% $MeCl_2$ in pentane	2,4,2',4' -tetrachlorobiphenyl	20
6. 10 ml 40% $MeCl_2$ in pentane	1,2,4-trimethylbenzene	116
	2,4,2',4' -tetrachlorobiphenyl	101

Alumina Column Cleanup

The selectivity of alumina adsorption chromatography columns for PAHs was evaluated. The alumina columns were prepared as described in Section 5. Elution volumes for ST INTF 1 compounds were determined using 10% $MeCl_2$ in pentane as the eluent. Elution volumes for PAHs, ST INTF 2, and DOP were determined using 100% $MeCl_2$ as the eluent. The resulting fractions were analyzed by UV spectrometry as described earlier.

Results of these analyses indicated that the elution volume for ST INTF 1 compounds was from 5 to 15 mL using the 10% $MeCl_2$ in pentane eluent while PAHs were completely retained on the column for the total elution volume of 50 mL. When using 100% $MeCl_2$ as the eluent, PAHs showed two maxima. One maximum occurred at an elution volume between 15 and 25 mL and the second maximum between 35 and 45 mL. However, there was still some absorbance indicated for the tenth 5 mL fraction for PAHs. DOP and ST INTF 2 compounds appeared to be totally retained on the alumina column with an elution of 50 mL of $MeCl_2$.

Because PAHs were partially retained after eluting with 50 mL of $MeCl_2$, the above experiments were repeated using an elution volume of 60 mL of $MeCl_2$. Results of these experiments indicated that PAHs were eluted at a total elution volume of 55 mL and DOP and ST INTF 2 compounds were completely retained. Elution with 30 mL of diethyl ether was necessary to elute the DOP and ST INTF 2 compounds from alumina.

GC analysis was conducted on the later eluting PAH fractions to determine which compounds were being retained. Results of these analyses indicated the PAHs in the second maximum were primarily benzo(b)fluoranthene, indeno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene with a small amount of benzo(a)pyrene.

On the basis of these results, alumina was selected as the adsorbent of choice since both polar and nonpolar (e.g., PCB) components are separated from the PAHs using this approach.

Evaluation of PAH Recoveries from Alumina and Silica Gel Column Cleanup

Recoveries of PAHs were determined for the alumina column cleanup method outlined above and for the silica gel cleanup method specified in U.S. EPA Method 610. The 60-mL alumina column PAH fraction and the 25-mL silica gel PAH fraction were collected and concentrated to 1 mL using Kuderna-Danish evaporation. In addition, 1 mL of the original PAH sample solution (10^{-5} M) used in the column cleanup was diluted to 60 mL with $MeCl_2$ and concentrated in the same manner in order to determine if any losses occurred during the concentration step.

PAH recovery was determined by capillary column GC/FID (30 meter SE-52 capillary column) using a Spectra-Physics SP4000 data system. Peak areas obtained for the alumina and silica gel PAH fractions and the diluted/concentrated PAH sample were compared to the peak areas obtained for the original 10^{-5} M PAH solution to determine PAH recovery. The alumina and silica gel column cleanup methods were conducted in duplicate and the dilution/concentration solvent reduction procedure was conducted in triplicate. Results of these analyses are shown in Table 14.

The above experiments indicate that there is no loss of PAHs during the concentration step involving Kuderna-Danish evaporation and recovery of PAHs from the silica gel column is good. Recovery of PAHs from the alumina column cleanup method appears to be quite good except for naphthalene, acenaphthylene and benzo(k)fluoranthene.

The data from Table 14 also indicate that possibly naphthalene and acenaphthylene were eluting from the column before the PAH fraction is collected. Thus, an earlier cut was needed to quantitatively collect these compounds.

Experiments were conducted in which the alumina column cleanup method was applied to a 10^{-5} M solution of naphthalene, acenaphthylene, benzo(k)fluoranthene and the ST INTF 1 solution, with fractions collected at appropriate intervals. These fractions were reduced in volume by Kuderna-Danish evaporation and analyzed by GC as described earlier. Results of these analyses are shown in Table 15.

Data from Table 15 show that excellent recovery for PAHs can be achieved by collecting the PAH fraction following the elution of only 30 mL of 5% $MeCl_2$ in pentane rather than the 40 mL volume previously employed. Employing this scheme still results in the separation of ST INTF 1 compounds from PAHs. PAH cleanup using the alumina LC column method was chosen as the preferred method, since both polar and nonpolar interferences can be separated from the PAHs and quantitative recovery of the PAHs is obtained.

Based on the above results, an alumina LC separation scheme for PAHs was formulated as follows:

- Following the sample addition step, elute with 30 mL of 5% $MeCl_2$ in pentane. This fraction contains the nonpolar compounds.

- Elute with 60 mL of $MeCl_2$. This fraction contains the PAHs separated from the DOP and ST INTF 2 compounds.

This alumina cleanup scheme was evaluated using PAHs, ST INTF 1 (nonpolar interferences) and ST INTF 2 (polar interferences). A one-milliliter solution containing 25 µg of each ST INTF 1 and ST INTF 2 compound and 10^{-8} moles (1-3 µg) of each PAH in cyclohexane was carried through the cleanup scheme in triplicate. The PAH fraction was concentrated to exactly five milliliters and the concentration of total PAH was determined from a calibration curve using standard solutions containing equal quantities of each of the 16 PAHs in cyclohexane. These data, shown in Table 16, demonstrate that the cleanup step is effective in excluding both nonpolar compounds (e.g., alkylbenzenes, PCBs) and polar compounds (e.g., nitrogen-heterocyclics,

TABLE 14. PAH RECOVERY USING COLUMN CLEANUP METHODS

Compound	Percent Recovery from Given Operation Solvent Concentration Only	Alumina Cleanup and Solvent Concentration	Silica Gel Cleanup and Solvent Concentration
Naphthalene	105 ±7[(a)]	37 ±35	92 ±6
Acenaphthylene	104 ±2	17 ±6	95 ±7
Acenaphthene	99 ±6	80 ±0.1	94 ±6
Fluorene	102 ±8	102 ±4	94 ±9
Phenanthrene	99 ±6	116 ±1	94 ±13
Anthracene	102 ±6	106 ±2	94 ±14
Fluoranthene	101 ±4	117 ±3	96 ±16
Pyrene	97 ±4	115 ±3	96 ±16
Benzo(a)anthracene	97 ±3	111 ±4	95 ±17
Chrysene	97 ±3	114 ±6	96 ±16
Benzo(b)fluoranthene	97 ±3	116 ±11	91 ±13
Benzo(k)fluoranthene	95 ±1	(b)	95 ±13
Benzo(a)pyrene	96 ±2	112 ±5	91 ±12
Indeno(1,2,3-cd)pyrene	97 ±1	110 ±2	91 ±11
Dibenzo(a,h)anthracene	98 ±1	99 ±7	93 ±12
Benzo(ghi)perylene	96 ±1	118 ±3	93 ±11

(a) Average ± standard deviation for duplicate samples for column 1 and triplicate samples for column 2 and 3.

(b) Computer integration problem - evaluation of this compound individually indicated quantitative recovery.

TABLE 15. EVALUATION OF ALUMINA COLUMN CLEANUP FOR SELECTED PAHS AND NONPOLAR COMPOUNDS

Fraction	Nonpolar Compounds		PAH	
	Compounds	% Eluted	Compound	% Eluted
1. 20 ml 5 % $MeCl_2$/pentane	1,2,4-trimethylbenzene 1,2,4-trichlorobenzene hexachlorobenzene 2,4,2',4'-tetrachlorobiphenyl 2,4,6,2',4',6'-hexachlorobiphenyl	94 96 100 59 96	none	-
2. 10 ml 5 % $MeCl_2$/pentane	2,4,2',4'-tetrachlorobiphenyl	32	none	-
3. 10 ml 5 % $MeCl_2$/pentane	none	-	naphthalene acenaphthylene	88 68
4. 10 ml $MeCl_2$	none	-	naphthalene acenaphthylene	22 29
5. 10 ml $MeCl_2$	none	-	benzo(k)fluoranthene	75
6. 40 ml $MeCl_2$	none	-	benzo(k)fluoranthene	42

TABLE 16. RESULTS FOR ALUMINA COLUMN CLEANUP OF COMBINED STANDARDS

Sample*	Absorbance	Apparent Total PAH Concentration ($\underline{M} \times 10^6$)	Percent Recovery (%)
Replicate 1	0.247	37	116
Replicate 2	0.216	30	94
Replicate 3	0.235	35	109
Average	0.232	34	106
ST PAH (32×10^{-6} M)	0.225	32	-

* One-milliliter solution containing 25 μg of each ST INTF 1 (nonpolar) and ST INTF 2 (polar) compound and 10^{-8} moles of each PAH was applied to the column. PAH fraction was concentrated to five mL.

phthalates). Further evaluation of the cleanup scheme was conducted using 2,6-di-t-butyl-p-cresol (BHT) and dibenzothiophene. BHT was not eluted from the alumina, even with 100% ether, whereas dibenzothiophene was eluted in the PAH fraction.

Based on these data, the alumina cleanup scheme appears to successfully eliminate most potential interferences although the PAH fraction will still contain sulfur heterocycles, such as dibenzothiophene, and possibly biphenyl (but not PCBs). These compounds therefore may interfere in the subsequent determinative step. Alkylated PAHs will elute in the PAH fraction, based on previous experience with the alumina cleanup procedure.

EVALUATION OF "CHANNEL" THIN LAYER CHROMATOGRAPHY (TLC)

This approach to PAH determination has been reported in the literature (16). Since both sample cleanup and analysis are achieved in a single step, this approach was believed to potentially offer reduced analytical costs.

Experiments for the TLC method involved spotting plates with the ST INTF 1, ST INTF 2, and ST PAH (10^{-3} M) solutions as well as various concentrations of anthracene to determine if any interferences occur for PAHs and whether or not band length is proportional to concentration. Results of these experiments are listed in Tables 17 through 19.

Evaluation of the TLC data indicated that ST INTF 1 compounds are not visible at a concentration level of 100 μg/mL on alumina or silica gel plates at 254 nm and 366 nm and would not interfere with any measurement of PAHs. Also, ST INTF 2 compounds do not move on silica gel and have a significantly different R_f value than PAHs on alumina plates. Therefore, ST INTF 2 compounds also would not interfere with a measurement for PAHs.

However, as can be seen from the data obtained for spotting the ST PAH solutions and anthracene alone, over a range of concentrations this TLC technique does not yield linear response. Also the technique is not sufficiently reproducible to be the basis for a screening method for PAHs without substantial modification. Therefore, the method was not investigated further.

VALIDATION OF SCREENING METHOD FOR PAHS

Based on the results presented above, a screening method for determining PAHs in wastewater was selected. This method, presented in detail in Appendix B, consists of the following steps:

(1) Extraction of the sample (1 liter) with a single aliquot (150 mL) of $MeCl_2$. Only 100 mL of the $MeCl_2$ is collected so as to reduce susceptibility to emulsion problems.

TABLE 17. CHANNEL TLC ON ALUMINA PLATES

Solution Spotted	Amount Spotted, µl	Detection at 254 nm Band Length, mm	R_f	Detection at 366 nm Band Length, mm	R_f
ST INTF 1 (1 µg/mL)	5	NV(a)	-	NV	-
ST INTF 1 (100 µg/mL)	10	NV	-	NV	-
ST INTF 2 (1 µg/mL)	5	NV	-	V(b)	0.00
ST INTF 2 (100 µg/mL)	10	23 9	0.11 0.47	23 9	0.11 0.47
ST PAH (10^{-5} M)	1	NV	-	NV	-
ST PAH (10^{-5} M)	10	10	0.79	35	0.79
ST PAH (10^{-5} M)	20	7	0.78	33	0.79

(a) NV = not visible
(b) V = visible

TABLE 18. CHANNEL TLC ON SILICA GEL PLATES

Solution Spotted	Amount Spotted, µl	Detection at 254 nm Band Length, mm	Detection at 254 nm R_f	Detection at 366 nm Band Length, mm	Detection at 366 nm R_f
ST INTF 1 (1 µg/mL)	5	NV (a)	-	NV	-
ST INTF 1 (100 µg/mL)	10	NV	-	NV	-
ST INTF 2 (1 µg/mL)	5	NV	-	V(b)	0.00
ST INTF 2 (100 µg/mL)	10	V	0.00	V	0.00
ST PNA (10^{-5} M)	5	NV	-	25	0.62
ST PNA (10^{-5} M)	10	7	0.56	21	0.56
ST PNA	20	11	0.55	20	0.5

(a) NV = not visible
(b) V = visible

TABLE 19. CHANNEL TLC OF ANTHRACENE ON ALUMINA PLATES

	Volume of Anthracene Spotted, µL	Amount of Anthracene Spotted, µg	Band Length, mm, at Selected Wavelength	
			254 nm	366 nm
Plate 1				
	10	1.8	14	19
	20	3.6	17	22
	30	5.4	24	25
	40	7.1	21	23
Plate 2				
	10	1.8	10	17
	20	3.6	12	19
	30	5.4	16	23
	40	7.1	21	25
Plate 3				
	10	1.8	14	17
	5	0.9	15	16
	2	0.4	11	13
	1	0.1	9	10
Plate 4				
	10	1.8	13	20
	5	0.9	12	20

(2) Drying (sodium sulfate) and Kuderna-Danish concentration of the extract.

(3) Alumina cleanup.

(4) Measurement of total UV absorbance, relative to a fluoranthene calibration standard, using a filter photometer.

The total UV determinative procedure was judged to be superior to either the fluorescence or "channel" TLC methods because of great variability in response between the PAH compounds of interest for the latter methods. Bias (inaccuracy) of ± 1000% or greater may be observed for the latter methods, depending on the specific PAH compounds present. By comparison, the total UV method bias should not exceed ± 100%, based on the response ratios determined for the priority pollutant PAHs.

The proposed method was initially applied to reagent water and two wastewaters, spiked at various levels with equimolar concentrations of all 16 PAHs. These results are presented in Tables 20 and 21. In all cases, reproducibility and recovery were excellent and therefore the proposed method was considered suitable for detailed validation.

Method validation consisted of (1) determination of the method detection limit (MDL) for the screening method using the U.S. EPA protocol given in Appendix A, and (2) comparison of analytical results obtained for relevant water samples, unspiked and spiked at various levels, using the PAH screening method and the U.S. EPA Method 610.

Method Detection Limit (MDL) Determination

The MDL for the PAH screening method was determined according to the protocol given in Appendix A. The spiked aliquots contained equimolar concentrations of all 16 priority pollutant PAHs. The process blank value (reagent water process blank) was subtracted from all the values prior to calculating the MDL, since this calculation procedure is recommended in the analytical method.

The MDL data for reagent water and three relevant water samples are presented in Table 22. The MDL values for the various water types are essentially the same (approximately 4 μg/L). These results seem reasonable, based on a reproducible process blank level of 2.5 μg/L and the MDL of 4 μg/L is considered to be satisfactory compared to alternative methods, such as U.S. EPA Method 610. Although U.S. EPA Method 610 can detect less than 4 μg/L of most individual PAHs, the detection limit, in terms of total PAH, will be higher (poorer) when a variety of PAHs are present in a given sample.

Comparison of U.S. EPA Method 610 and PAH Screening Method

Aliquots of distilled water, POTW secondary effluent, a final effluent from a coking operation, and a refinery effluent were extracted and

TABLE 20. DETERMINATION OF PAH IN DISTILLED WATER BY TOTAL UV METHOD

Sample	Total PAH Spike Level(a)		Absorbance				Total PAH Concentration Found		Average Percent Recovery ± SD (c)
	($\underline{M} \times 10^6$)	µg/L(b)	Rep. 1	Rep. 2	Rep. 3	Average ± SD	($\underline{M} \times 10^6$)	µg/L	
Unspiked	0	0	0.041	0.045	0.042	0.043 ± 0.002	0.04	8	—
Spike Level 1	0.08	16	0.091	0.107	0.137	0.112 ± 0.023	0.11	22	88 ± 22
Spike Level 2	0.32	64	0.301	0.235	0.331	0.289 ± 0.049	0.33	65	91 ± 15
Spike Level 3	0.80	160	0.635	0.617	0.635	0.629 ± 0.010	0.75	150	89 ± 1.4

(a) Equimolar mixture of all 16 priority pollutant PAHs.
(b) Average molecular weight of 200 is assumed.
(c) Corrected for background PAH level.
SD = Standard deviation.

TABLE 21. RESULTS FOR DETERMINATION OF PAH IN WASTEWATER USING THE TOTAL UV METHOD

Sample	Total PAH Spike Concentration(a)		Absorbance				Total PAH Found		Average Percent Recovery ± SD(c)
	$\underline{M} \times 10^6$	µg/L(b)	Rep. 1	Rep. 2	Rep. 3	Average ± SD	$\underline{M} \times 10^6$	µg/L(b)	
POTW Sewage (Columbus)	0	0	0.030	0.020	0.021	0.024 ± 0.005	0.02	4	—
POTW Sewage (Columbus)	0.16	32	0.169	0.159	0.153	0.160 ± 0.008	0.16	32	88 ± 4.4
Coking Effluent	0	0	0.038	0.041	0.043	0.041 ± 0.002	0.04	8	—
Coking Effluent	0.16	32	0.171	0.158	0.200	0.176 ± 0.021	0.18	35	84 ± 10

(a) Spiked with equimolar mixture of all 16 priority pollutant PAHs.
(b) Assuming an average molecular weight of 200.
(c) Corrected for background PAH level.
SD = Standard deviation.

TABLE 22. METHOD DETECTION LIMIT FOR PAH SCREENING METHOD
IN TERMS OF FLUORANTHENE EQUIVALENTS

Sample	Spike Level (µg/L)[a]	Background Level (µg/L)	Amount Found (µg/L)							Average	SD	MDL	Percent Recovery
			Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7				
Reagent Water	5.5	2.4	6.6	8.4	7.5	7.7	8.4	9.4	9.3	8.2			
			(4.2)[b]	(6.0)	(5.1)	(5.3)	(6.0)	(7.0)	(6.9)	(5.8)	1.1	3.5	105
Coking Effluent	5.5	3.2	7.0	7.9	9.1	7.8	6.6	7.3	8.1	7.7			
		(0.8)	(4.6)	(5.5)	(6.7)	(5.4)	(4.2)	(6.9)	(5.7)	(5.3)	1.2	3.1	82
Refinery Effluent	5.5	11.0	19.2	17.3	21.1	16.8	18.7	16.8	18.7	18.4			
		(8.6)	(16.8)	(14.9)	(18.7)	(14.4)	(16.3)	(14.4)	(16.3)	(16.0)	1.6	4.9	135

(a) Spiked with an equimolar mixture of all 16 priority pollutant PAHs.

(b) Values in parenthesis are corrected for process blank level of 2.4 mL/L. These blank corrected data were used for calculation of MDL.

SD = Standard deviation.

MDL = Method Detection Limit.

cleaned up according to the procedure in Appendix B. Three aliquots of each sample unspiked and spiked at each of two concentration levels were extracted. The extracts were analyzed by the PAH screening method and then exchanged into acetonitrile and analyzed by the HPLC approached described in U.S. EPA Method 610. One extract of each sample (unspiked) was analyzed by GC/MS to confirm component identifies.

The results of the U.S. EPA Method 610 analyses for the three samples are shown in Tables 23-26. In most cases, with the exception of benzo(k)fluoranthene, the recovery was greater than 75% at both the high and low spike levels. The process blanks contained no detectable level of any of the 16 priority pollutant PAH compounds.

The values obtained using the screening method are compared to the U.S. EPA Method 610 results in Table 27 for all four water types. The values for the screening method are consistently higher than the U.S. EPA Method 610 results. This positive bias results from the use of fluoranthene as the calibration standard. Since the molar absorptivity of fluoranthene is slightly less than the average molar absorptivity of the 16 PAH compounds, the absorbance of the PAH mixed standard used to spike the samples is greater than the fluoranthene standard. This factor is demonstrated by comparing the actual spike level (first column of Table 27) to the spike level in terms of "fluoranthene equivalents".

While this bias can be significantly reduced by selecting a different PAH spiking standard, this procedure would not be effective in a real world situation (i.e., when the levels of individual PAH compounds are not known). In practice, the amount of bias will not be known and will vary from sample to sample, within the relative sensitivity factors (approximately ± 100% relative to fluoranthene) of the various PAH compounds (last column of Table 10). In certain cases where the major PAH species is known, the amount of bias can be minimized by calibrating with that particular PAH species. This process is allowed in the detailed method description given in Appendix B.

The background level of the distilled water sample was approximately 2.5 μg/L while the POTW, coking effluent, and refinery effluent samples had slightly higher backgrounds due to the presence of PAH. The refinery effluent gave a background level of 11.8 μg/L. In practice, the screening method blank consistently gives a background level of approximately 2.0-2.5 μg/L. The method description suggests that results be corrected for method blank in order to reduce the degree of positive bias for the method. This amount of background may be due to contamination of the sample with trace amounts of UV absorbing material, such as phthalates, following the cleanup step.

GC/MS analysis of the wastewater extracts confirms that traces of phthalates (representing less than 5 μg/L in the wastewater sample) are present in the extracts. Trace quantities of phenanthrene and naphthalene were identified in the refinery effluent and the POTW effluent. Methylthiobenzene was also identified in the refinery effluent. Naphthalene, methylnaphthalenes, dimethylnaphthalenes, phenanthrene, and pyrene were detected in the POTW secondary effluent.

TABLE 23. RECOVERY OF PAH FROM SPIKED DISTILLED WATER USING U.S. EPA METHOD 610

	Spike Level (μg/ℓ)	Amount Recovered (μg/ℓ)			Average Percent Recovery	Relative Standard Deviation(%)	Spike Level (μg/ℓ)	Amount Recovered (μg/ℓ)			Average Percent Recovery	Relative Standard Deviation(%)
		Rep 1	Rep 2	Rep 3				Rep 1	Rep 2	Rep 3		
Naphthalene	0.68	(a)	(a)	(a)	—	—	0.13	(a)	(a)	(a)	—	—
Acenaphthylene	0.89	(a)	(a)	(a)	—	—	0.17	(a)	(a)	(a)	—	—
Acenaphthene	0.85	(a)	(a)	(a)	—	—	0.17	(a)	(a)	(a)	—	—
Fluorene	0.84	0.72	0.60	0.57	75	13	0.17	(a)	(a)	(a)	—	—
Phenanthrene	0.91	0.69	0.71	0.60	73	9	0.18	0.16	0.12	0.11	70	22
Anthracene	0.90	0.68	0.73	0.76	81	6	0.18	0.19	0.25	0.16	112	23
Fluoranthene	1.20	0.94	1.29	1.16	94	16	0.24	0.29	0.22	0.23	102	15
Pyrene	1.11	0.85	1.00	0.89	82	8	0.22	0.25	0.16	0.21	96	22
Benzo(a)anthracene	1.23	1.10	1.50	1.39	108	16	0.25	0.21	0.20	0.18	79	8
Chrysene	1.36	1.03	1.22	1.20	85	9	0.27	0.31	0.25	0.24	98	14
Benzo(b)fluoranthene	1.41	1.15	1.50	1.40	96	13	0.28	0.22	0.21	0.18	71	10
Benzo(k)fluoranthene	1.28	0.60	0.82	0.89	55	20	0.26	0.15	0.14	0.12	54	14
Benzo(a)pyrene	1.17	0.97	1.18	1.21	96	12	0.23	0.22	0.20	0.19	88	8
Dibenzo(a,h)anthracene	1.42	1.36	1.55	1.45	102	7	0.28	0.27	0.28	0.29	98	4
Benzo(ghi)perylene	1.49	1.31	1.45	1.40	93	5	0.30	0.31	0.35	0.37	115	3
Indeno(1,2,3-cd)pyrene	1.46	1.29	1.33	1.31	90	2	0.29	0.34	0.32	0.29	110	7

(a) Spike level below detection limit.

TABLE 24. RECOVERY OF PAH FROM SPIKED POTW WASTEWATER USING U.S. EPA METHOD 610

	Background Level (µg/L)(a)	Spike Level (µg/L)	Amount Recovered (µg/L)			Average Percent Recovery	Relative Standard Deviation(%)	Spike Level (µg/L)	Amount Recovered (µg/L)			Average Percent Recovery	Relative Standard Deviation(%)
			Rep 1	Rep 2	Rep 3				Rep 1	Rep 2	Rep 3		
Naphthalene	ND	1.26	1.11	1.08	0.44	75	28	0.13	(b)	(b)	(b)	—	—
Acenaphthylene	ND	1.68	(b)	(b)	(b)	—	—	0.17	(b)	(b)	(b)	—	—
Acenaphthene	ND	1.69	1.97	1.86	1.69	109	8	0.17	(b)	(b)	(b)	—	—
Fluorene	ND	1.68	1.37	1.28	1.23	77	5	0.17	(b)	(b)	(b)	—	—
Phenanthrene	0.19	1.82	2.07	1.93	1.90	108	5	0.18	0.21	0.16	0.17	106	14
Anthracene	ND	1.78	1.76	1.70	1.58	94	5	0.18	0.31	0.23	0.22	144	19
Fluoranthene	0.06	2.40	2.32	2.13	2.52	97	8	0.24	0.43	0.32	0.32	148	18
Pyrene	ND	2.21	2.27	1.77	2.80	103	23	0.22	0.34	0.24	0.22	121	26
Benzo(a)anthracene	0.03	2.46	2.73	2.61	3.49	120	16	0.25	0.24	0.26	0.18	92	20
Chrysene	ND	2.71	2.54	2.29	3.04	97	15	0.27	0.15	0.18	0.20	65	14
Benzo(b)fluoranthene	ND	2.83	2.83	2.63	3.01	100	7	0.28	0.29	0.30	0.27	101	4
Benzo(k)fluoranthene	ND	2.56	1.11	1.20	2.09	57	37	0.26	0.06	0.06	0.07	25	12
Benzo(a)pyrene	ND	2.34	2.06	1.94	2.56	94	15	0.23	0.23	0.23	0.22	96	3
Dibenzo(a,h)anthracene	ND	2.83	3.01	2.78	3.53	110	12	0.28	0.31	0.32	0.31	112	1
Benzo(ghi)perylene	ND	2.98	2.85	2.73	3.94	106	21	0.30	0.35	0.35	0.33	114	4
Indeno(1,2,3-cd)pyrene	ND	2.91	2.88	2.76	2.65	95	4	0.29	0.28	0.31	0.28	100	6

ND = not detected.

(a) Average of three replicates.

(b) Spike level below detection limit.

TABLE 25. RECOVERY OF PAH FROM SPIKED COKING EFFLUENT WASTEWATER USING U.S. EPA METHOD 610

	Background Level (µg/L)(a)	Spike Level (µg/L)	Amount Recovered (µg/L)			Average Percent Recovery	Relative Standard Deviation(%)	Spike Level (µg/L)	Amount Recovered (µg/L)			Average Percent Recovery	Relative Standard Deviation(%)
			Rep 1	Rep 2	Rep 3				Rep 1	Rep 2	Rep 3		
Naphthalene	0.30	1.26	1.43	ND	1.54	118	5	0.13	0.46	0.53	0.35	406	9
Acenaphthylene	ND	1.68	(b)	(b)	(b)	—	—	0.17	(b)	(b)	(b)	—	—
Acenaphthene	0.50	1.69	2.00	2.35	2.69	139	15	0.17	(b)	(b)	(b)	—	—
Fluorene	ND	1.68	1.51	1.77	1.83	101	10	0.17	(b)	(b)	(b)	—	—
Phenanthrene	0.20	1.82	2.28	2.16	2.97	136	18	0.18	0.24	0.26	0.41	160	30
Anthracene	0.04	1.78	1.92	1.88	2.28	114	11	0.18	0.23	0.23	0.25	132	4
Fluoranthene	0.09	2.40	2.54	2.15	2.51	100	9	0.24	0.29	0.31	0.32	128	5
Pyrene	ND	2.21	2.04	1.75	1.99	87	8	0.22	0.23	0.24	0.21	103	7
Benzo(a)anthracene	0.06	2.46	2.96	2.81	2.84	117	3	0.25	0.26	0.27	0.28	111	4
Chrysene	ND	2.71	2.75	2.46	2.35	93	8	0.27	0.23	0.25	0.27	92	9
Benzo(b)fluoranthene	0.03	2.83	2.85	2.94	2.69	100	4	0.28	0.29	0.31	0.31	107	5
Benzo(k)fluoranthene	0.04	2.56	0.51	0.87	0.49	24	35	0.26	0.02	0.03	0.02	9	18
Benzo(a)pyrene	0.05	2.34	2.09	2.01	2.08	88	2	0.23	0.24	0.25	0.25	104	2
Dibenzo(a,h)anthracene	0.05	2.83	3.03	3.14	2.87	106	5	0.28	0.27	0.30	0.31	103	7
Benzo(ghi)perylene	ND	2.98	3.07	2.63	2.87	96	11	0.30	0.33	0.37	0.35	117	6
Indeno(1,2,3-cd)pyrene	0.04	2.91	2.84	2.78	2.55	93	6	0.29	0.28	0.29	0.30	98	5

ND = not detected.

(a) Average of three replicates.

(b) Spike level below detection limit.

TABLE 26. RECOVERY OF PAH FROM SPIKED REFINERY EFFLUENT USING U.S. EPA METHOD 610

Compound	Spike Level (µg/L)	Amount Recovered (µg/L) Rep. 1	Rep. 2	Rep. 3	Average Percent Recovered	Relative Standard Deviation (%)	Spike Level (µg/L)	Amount Recovered (µg/L) Rep. 1	Rep. 2	Rep. 3	Average Percent Recovered	Relative Standard Deviation (%)
Naphthalene	1.26	5.99	6.40	6.90	(a)	7	0.13	5.64	6.70	4.79	(a)	17
Acenaphthylene	1.68	0.95	1.38	1.08	68	19	0.17	(b)	(b)	(b)	—	—
Acenaphthene	1.69	1.69	1.87	1.84	107	5	0.17	(b)	(b)	(b)	—	—
Fluorene	1.68	1.74	1.66	1.40	95	11	0.17	(b)	(b)	(b)	—	—
Phenanthrene	1.82	1.88	1.66	2.18	103	14	0.18	0.50	0.48	0.39	254	13
Anthracene	1.78	1.72	1.77	1.67	97	3	0.18	0.14	0.17	0.13	81	14
Fluoranthene	2.40	2.44	2.32	2.53	101	4	0.24	0.24	0.21	0.23	94	7
Pyrene	2.21	1.81	1.86	1.98	85	9	0.22	0.18	0.13	0.17	73	16
Benzo(a)anthracene	2.46	2.15	2.08	2.69	94	14	0.25	0.23	0.20	0.25	91	11
Chrysene	2.71	2.83	2.62	2.48	98	7	0.27	0.23	0.18	0.25	81	16
Benzo(b)fluoranthene	2.83	2.79	2.73	2.57	95	4	0.28	0.25	0.27	0.23	89	8
Benzo(k)fluoranthene	2.56	1.14	1.20	1.05	44	7	0.26	0.11	0.13	0.09	42	18
Benzo(a)pyrene	2.34	2.14	2.27	2.35	96	5	0.23	0.20	0.23	0.18	88	12
Benzo(a,h)anthracene	2.83	2.95	2.20	2.36	88	16	0.28	0.23	0.29	0.20	86	19
Benzo(ghi)perylene	2.98	2.73	2.60	3.08	94	9	0.30	0.26	0.21	0.29	84	16
Indeno(1,2,3-cd)pyrene	2.91	3.23	2.09	2.40	88	23	0.29	0.24	0.32	0.23	91	19

(a) An average of 6.5 µg/L of naphthalene was found in unspiked sample.
(b) Spike level below detection limit.

TABLE 27. COMPARISON OF SCREENING METHOD TO U.S. EPA METHOD 610 FOR VARIOUS WATER SAMPLES

Sample	PAH Spike Level (µg/L)	Spike Level in Fluoranthene Equivalents (µg/L)	Total PAH Found using Method 610 (µg/L)	Total PAH Found using Surrogate Method Fluoranthene Equivalents (µg/L)	Average Percent Recovery(a) ± SD	
					U.S. EPA Method 610	Screening Method(b)
Reagent Water	18.1	27.6	12.7	26.3 (21.8)(c)		
"	18.1	27.6	14.9	27.9 (25.4)	77 ± 8	96 ± 19
"	18.1	27.6	14.2	36.4 (31.9)		
"	3.6	5.5	2.9	8.4 (5.9)		
"	3.6	5.5	2.7	7.9 (5.4)	76 ± 6	99 ± 8
"	3.6	5.5	2.6	7.5 (5.0)		
Method Blank	—	—	—	2.5		
POTW	36.2	55.2	32.9	45.8 (43.3)		
"	36.2	55.2	30.7	43.2 (40.7)	90 ± 9	76 ± 3
"	36.2	55.2	36.7	45.8 (43.3)		
"	3.6	5.5	3.5	8.6 (6.1)		
"	3.6	5.5	3.2	6.8 (4.3)	75 ± 6	92 ± 12
"	3.6	5.5	3.1	8.1 (5.6)		
"	—	—	0.3	2.5 (0.0)		
"	—	—	0.2	2.9 (0.4)	—	—
"	—	—	0.3	3.0 (0.5)		
Coking Effluent	36.2	55.2	33.8	48.6 (46.1)		
"	36.2	55.2	31.7	46.8 (44.3)	87 ± 3	78 ± 4
"	36.2	55.2	33.0	45.0 (42.5)		
"	3.6	5.5	3.4	8.3 (5.9)		
"	3.6	5.5	3.6	7.9 (5.4)	61 ± 6	97 ± 15
"	3.6	5.5	3.8	10.4 (7.9)		
"	—	—	0.7	3.4 (0.9)		
"	—	—	1.7	3.6 (1.1)	—	—
"	—	—	1.8	3.6 (1.1)		
Refinery Effluent	36.2	55.2	38.2	58.1 (55.5)	85 ± 3	86 ± 8
"	36.2	55.2	36.7	52.6 (50.1)	85 ± 3	86 ± 8
"	36.2	55.2	38.6	62.0 (59.5)		
Refinery Effluent	3.6	5.5	8.4	17.5 (15.0)		
"	3.6	5.5	9.5	17.3 (14.8)	43 ± 12	135 ± 32
"	3.6	5.5	7.4	20.6 (18.1)		
Refinery Effluent	—	—	5.5	11.0 (8.5)		
"	—	—	7.0	10.6 (8.1)	—	—
"	—	—	8.3	11.5 (9.0)		

(a) Corrected for unspiked sample.
(b) Fluoranthene equivalent spike value was used to calculate recovery.
(c) Values in parenthesis are corrected for method blank.
SD = Standard deviation.

The PAH screening method results and U.S. EPA Method 610 results, given in Table 24, were subjected to linear regression analysis to determine the degree of correlation between the two methods. Screening method data were entered as the "Y" values and U.S. EPA Method 610 were entered as the "X" values. The slope, intercept, correlation coefficient, and R-squared (residual) values were calculated for each water type as well as for the data set as a whole. The results of these regression analyses are presented in Table 28.

The slope values were approximately 1.3, with the exception of reagent water, which is indicative of a positive bias (~30%) for the screening method. The reasons for this bias are discussed above. The intercept values were approximately 3 μg/L, which is approximately equal to the method detection limit. This result indicates that the relative bias in the method is constant over the concentration range tested (i.e., there is not a large fixed bias inherent in the method). The correlation coefficients were somewhat better in wastewater than in distilled water, and are considered to be satisfactory in all cases. The R-squared values were always >95%, indicating that the data points fall relatively close to the regression line. The regression plot for the entire data set is shown in Figure 6.

It is important to recognize that these correlation data are rigorously valid only for the particular spiking scheme shown. If other combinations of PAHs are present, a different slope will be obtained for the regression line, although the other parameters (e.g., correlation coefficient, intercept) will not be greatly affected. These results indicate that the PAH screening method is precise and positively correlated with U.S. EPA Method 610, which is currently in use for the determination of priority pollutant PAHs in wastewater. An important consideration in the evaluation of these two methods is the analytical cost, since one of the primary objectives in the development of screening methods is to reduce the analytical costs associated with monitoring pollutants.

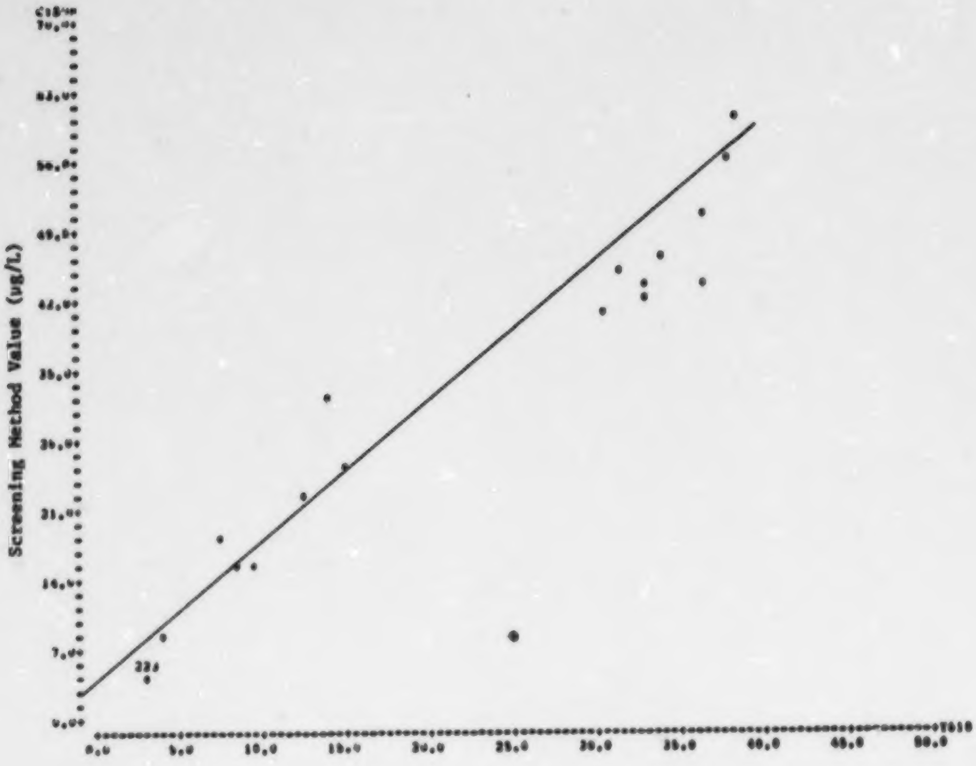
The PAH screening method requires considerably less time to conduct than does U.S. EPA Method 610. The sample extraction step involves a single extraction step with a fixed proportion (2/3) of the extract being recovered. This process reduces the problems with emulsions substantially since the emulsive interface does not need to be recovered. In addition, the instrument calibration, sample analysis, and data reduction steps are accomplished much more rapidly for the screening method, since only a single numerical value (total PAH concentration) rather than 16 individual concentration values is obtained, and the lengthy chromatographic analysis is eliminated. In addition, the time required to prepare reference standard solutions is greatly reduced. Only a single standard (fluoranthene) is required.

The PAH screening method utilizes considerably less expensive equipment than does U.S. EPA Method 610 ($5,000 vs. $25,000) and requires fewer materials and less trained personnel.

A potential use for the total UV approach, employed in the PAH screening method, is analysis of samples prior to GC/MS or HPLC determination. For example, the total UV approach could be used to screen sample extracts

TABLE 28. LINEAR REGRESSION ANALYSIS RESULTS FOR THE PAH SCREENING METHOD AND U.S. EPA METHOD 610

Water Type	Slope	Y-Intercept, µg/L	Correlation Coefficient	R-Squared (%)
All types	1.30	3.1	0.982	96
Reagent water	1.88	0.26	0.973	95
POTW effluent	1.22	1.5	0.996	99
Coking effluent	1.30	1.7	0.998	99
Refinery effluent	1.33	4.7	0.991	98



Method 610 Value (µg/L)

Figure 6. Regression analysis of screening method versus U.S. EPA Method 610 for all water types.

generated by U.S. EPA Method 610 (prior to HPLC analysis) to selectively eliminate low level samples and thereby reduce analytical costs.

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APPENDIX A

DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT

DEFINITION

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and determined from analysis of a sample in a given matrix containing analyte.

SCOPE AND APPLICATION

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific and well-defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

PROCEDURE

1. Make an estimate of the detection limit using one of the following:

    (a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

    (b) Three times the standard deviation of replicate instrumental measurements of the reagent water.

    (c) The area of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

    (d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interference concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interference). The interference concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

   (b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

   If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

   If the measured level of analyte is greater than five times the estimated detection limit, there are two options:

   (1) Obtain another sample containing a lower level of analyte in the same matrix if possible.

   (2) The untreated sample may be used for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each aliquot through the entire analytical method. Make all computations

according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This step will: (1) prevent repeating this entire procedure when the costs of analyses are high, and (2) ensure that the procedure is being conducted at the correct concentration. It is quite possible that an incorrect MDL could be calculated from data obtained at many times the real MDL and the level of analyte would be less than five times the calculated method detection limit. To ensure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

   (1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

   (2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left\{\left(\sum_{i=1}^{n} X_i^2\right) - \left(\sum_{i=1}^{n} X_i\right)^2 \Big/ n\right\}$$

$$S = (S^2)^{1/2}$$

where the x_i, $i=1$ to n are the analytical results in the final method reporting units obtained from the n sample aliquots and refers to the sum of the X values from $i=1$ to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,.99)} \quad (S)$$

where:

MDL = the method detection limit

$t_{(n-1,.99)}$ = the student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (X^2/df).

$$LCL = 0.69\ MDL$$

$$UCL = 1.92\ MDL$$

where LCL and UCL are the lower and upper 95% confidence limits respectively, based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike in the matrix at the calculates MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is formed by substituting the largest S^2 of the two into the numerator S and the other into the denominator S. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows:

$$\text{if} \quad \frac{S_A^2}{S_B^2} < 3.05,$$

then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{1/2}$$

if $\frac{S_A^2}{S_B^2} > 3.05$, respike at the last calculated MDL and

process the samples through the procedure starting with Step 4.

(c) Use the S_{pooled} as calculated in Step 7b to compute the final MDL according to the following equation:

$$MDL = 2.681\ (S_{pooled})$$

where 2.681 is equal to $t_{(12,\ = .99)}$.

(d) The 95% confidence limits for MDL derived in Step 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

$$LCL = 0.72\ MDL$$

$$UCL = 1.65\ MDL$$

where LCL and UCL are the lower and upper 95% confidence limits respectively, based on 14 aliquots.

TABLE OF STUDENT'S t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of Replicates	Degrees of Freedom (n-1)	$t_{(n-1,.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	0.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

REPORTING

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level in the sample was below the determined MDL or does not exceed 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

APPENDIX B

POLYNUCLEAR AROMATIC HYDROCARBONS

SCREENING METHOD

1. SCOPE AND APPLICATION

1.1 This method is a UV spectroscopic method applicable to the determination of total PAH compounds, including the 16 priority pollutant PAHs, in municipal and industrial discharges expressed as "fluoranthene equivalents". Most other PAH compounds and many sulfur heterocycles will also be detected; however, more polar materials (e.g., phthalates, phenols, and nitrogen heterocyclics) and PCBs will not interfere since these compounds are effectively removed in the cleanup step. U.S. EPA Methods 610 (1) or 625 (2) can be used to determine individual PAH components present in the sample.

1.2 The method detection limit (MDL), calculated using the U.S. EPA protocol (3) for total PAH is 3.5 μg/L, expressed as fluoranthene equivalents. Typical response factors for specific PAH compounds are given in Table B-1. The response factors (Table B-1) for the various PAH compounds should be confirmed using the instrument employed at each laboratory. These data are useful for estimating the range of responses expected for PAHs of interest in a particular application.

1.3 This procedure is intended for use as a cost effective screening method and is not intended to supplement the use of U.S. EPA Method 610 or 625. This method is not considered equivalent to either of these methods and is not intended as a replacement or approved alternate test procedure.

1.4 This method is restricted to use by or under the supervision of analysts experienced in water analysis and UV spectroscopy. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. SUMMARY OF METHOD

2.1 A measured volume of sample, approximately 1-liter, is extracted with a single 150 mL portion of methylene chloride using a separatory funnel. Only 100 mL of the methylene chloride extract is recovered, thereby reducing problems associated with recovering an emulsive interface layer. The methylene chloride extract is dried and concentrated to a volume of 10 mL or less. The solvent is exchanged to cyclohexane prior to cleanup. Following cleanup, ultraviolet (UV) detection is used for determination of total PAH expressed as fluoranthene equivalents.

3. INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware which lead to elevated background UV absorbance. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.5.

3.1.1 Glassware must be scrupulously cleaned (4). Clean all glassware as soon as possible after use by rinsing with the last solvent used. This step should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400°C for 15 to 30 minutes. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedure in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table B-2.

3.3 The extent of interferences that may be encountered using the UV absorbance technique has not been fully assessed. However, benzenes, PCBs, nitrogen heterocyclics, phenols, and phthalates have been shown not to interfere since they are removed by the column chromatography cleanup procedure. However, contamination of the sample after cleanup (e.g., with phthalate esters) may occur if great care is not taken.

4. SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (5-7) for the information of the analyst.

4.2 Many PAH which can be determined by this method have been tentatively classified as known or suspected human or mammalian carcinogens.

5. APPARATUS AND MATERIALS

5.1 Sampling equipment, for discrete or composite sampling

5.1.1 Grab sample bottle - Amber glass, 1-liter or 1-quart volume, fitted with screw caps lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional) - Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustraton only.)

5.2.1 Separatory funnel - 2000 mL, with Teflon stopcock.

5.2.2 Drying column - Chromatographic column 400 mm long x 19 mm ID with coarse frit

5.2.3 Concentrator tube, Kuderna-Danish - 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish - three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish - two-ball macro (Kontes K-569001-0219 or equivalent).

5.2.7 Vials - Amber glass, 10 to 15 mL capacity, with Teflon-lined screw caps.

5.2.8 Graduated cylinders - 100 mL and 1000 mL.

5.3 Boiling chips - approximately 10/40 mesh. Heat to 400°C for 30 minutes or extract (Soxhlet) with methylene chloride.

5.4 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

5.5 Balance - Analytical, capable of accurately weighing 0.0001 g.

5.6 Variable wavelength UV spectrometer equipped with a deuterium lamp capable of zero order transmission for total UV measurements (Perkin-Elmer Model 55B with Coleman Model 55-204 deuterium lamp and power supply or equivalent).

5.6.1 One matched pair micro-cuvettes, self masking with 10 mm path length.

5.6.2 Band pass filter (Corning number 7-54 or equivalent).

6. REAGENTS

6.1 Reagent water - Reagent water is defined as a water in which an interference is not observed at the method detection limit of each parameter of interest.

6.2 Sodium Thiosulfate - (ACS) Granular.

6.3 Cyclohexane, methylene chloride, and pentane - Pesticide quality or equivalent.

6.4 Fluoranthene - High purity (Aldrich or equivalent).

6.5 Sodium sulfate - (ACS) Granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

6.6 Alumina - 80-200 Mesh (Baker alumina, adsorption A-540 or equivalent). Before use, activate for at least 8 hours at 400°C, loosely covered with foil.

6.7 Stock standard solution of fluoranthene (1×10^{-3} $\underline{M}$) - Stock standard solution is prepared from pure standard material.

6.7.1 Prepare stock standard solution by accurately weighing 20.2 milligrams of pure fluoranthene. Dissolve the fluoranthene in pesticide quality methylene chloride, dilute to volume in a 100 mL volumetric flask. Larger volumes can be used at the convenience of the analyst.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing dilute calibration standards.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicate a problem.

7. CALIBRATION

7.1 The spectroscopic system is calibrated using an external standard technique.

7.2 External standard calibration procedure:

7.2.1 Prepare fluoranthene calibration standard at a minimum of three concentration levels by adding volumes of the stock solution to a volumetric flask and diluting to volume with methylene chloride. One of the concentrations should be near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Analyze each concentration of calibration standard and tabulate absorbance versus concentration (µg/mL). The results are used to prepare a working calibration curve. Data for an example calibration curve are listed in Table B-3. The instrument response above 0.5 absorbance units is non-linear, therefore all calibration standards and samples should be diluted so as not to exceed this range.

7.2.3 The working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared.

8. QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Using stock fluoranthene standard solutions, prepare concentrations in methylene chloride which are near the MDL.

8.2.2 Using a pipet, add 1.00 mL of the fluoranthene standard stock solution to each of a minimum of four 1000 mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery, (s), for the results. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using the appropriate data from Table B-2, determine the recovery and single operator precision expected for the method and compare these results to the values calculated in Section 8.2.3. If the data are not comparable, the analyst must review potential problem areas and repeat the test.

8.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance:

Upper Control Limit (UCL) = R + 3 s
Lower Control Limit (LCL) = R - 3 s

where R and s are calculated as in Section 8.2.3. The UCL and LCL can be used to construct control charts (8) that are useful in observing trends in performance.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternately, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly.

8.4 The laboratory is required to collect a portion of the samples in duplicate to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery does not fall within the control limits for method performance, the results reported in all samples processed as part of the same set must be qualified as described in Section 13.4. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Before processing any samples, the analyst should demonstrate through the analysis of a 1-liter aliquot of reagent water that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against laboratory contamination. The value obtained for the method process blank (reagent water handled in an identical manner as the samples) should not be greater than 4 µg/L. The process blank result should be subtracted from the sample result to obtain the final sample result. In general, the process blank has been found to be 2.5 ± 0.3 µg/L.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists as to the performance of the screening method, confirmatory techniques such as U.S. EPA Methods 610 or 625 must be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

9.1 Grab samples must be collected in glass containers. Conventional sampling practices (9) should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 The samples must be iced refrigerated at 4°C from the time of collection until extraction. PAHs are known to be light sensitive; therefore, samples, extracts and standards should be stored in amber or foil wrapped bottles in order to minimize photolytic decomposition. Fill the sample bottle and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample. U.S. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine (10). Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days, and analysis completed within 40 days of extraction.

10. SAMPLE EXTRACTION

10.1 Mark the water meniscus on the side of the sample bottle for later measurement of sample volume. Pour the entire sample into a 2-liter separatory funnel.

10.2 Add 150 mL of methylene chloride to the sample bottle, seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking for 2 minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect 100 mL of methylene chloride extract in a 100 mL graduated cylinder.

10.3 Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the Kuderna-Danish if the requirements of Section 8.2 are met.

10.4 Pour the extract through a drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the Kuderna-Danish concentrator. Rinse the graduated cylinder and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.5 Add 1 or 2 clean boiling chips to the evaporative flask and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the Kuderna-Danish apparatus on a hot water bath (60 to 65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reached 1 mL, remove the Kuderna-Danish apparatus and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw cap bottles and protected from light.

10.6 Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. CLEANUP AND SEPARATION

11.1 Alumina column cleanup is strongly recommended for all sample extracts, since all UV adsorbing compounds will otherwise interfere in the method. Therefore the cleanup step should be omitted only when the analyst is certain that UV adsorbing compounds other than PAH are not present in the sample at detectable levels.

11.2 Before the alumina cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. Add a 1 to 10 mL aliquot of sample extract (in methylene chloride) and a boiling chip to a clean Kuderna-Danish concentrator tube. Add 4 mL cyclohexane and attach a micro-Snyder column. Prewet the micro-Snyder column by adding 0.5 mL methylene chloride to the top. Place the micro-Kuderna-Danish apparatus on a boiling (100°C) water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 0.5 mL, remove the Kuderna-Danish apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum of cyclohexane. Adjust the extract volume to about 2 mL.

11.3 Alumina column cleanup for PAH[illegible]

11.3.1 Prepare a slurry of 1 [illegible] ctivated alumina in methylene chloride and place this in a 10 mm ID chromatography column. Gently tap the column to settle the alumina and elute the methylene chloride.

11.3.2 Preelute the column with 40 mL of pentane. Discard the eluate and just prior to exposure of the alumina layer to the air, transfer the entire 2 mL of cyclohexane sample extract onto the column, using an additional 2 mL of cyclohexane to complete the transfer.

11.3.3 Just prior to exposure of the alumina layer to the air, add 25 mL 5/95 methylene chloride/pentane (V/V) and continue elution of the column. Discard the eluate.

11.3.4 Elute the column with 60 mL of methylene chloride and collect the eluate in a 250 mL Kuderna-Danish flask equipped with a 10 mL concentrator tube. Elution of the column must not exceed a rate of 2 mL per minute.

11.3.5 Concentrate the collected fraction to 1.0 mL by Kuderna-Danish techniques as in Section 10.5, using methylene chloride to rinse the walls of the glassware. Proceed with total UV absorbance method.

12. TOTAL UV ABSORPTION METHOD

12.1 Place grating of UV spectrometer to zero order (transmitting white light) for total UV measurements. Adjust instrument for 100% transmission. Select absorption mode.

12.2 Position band-pass filter securely in front of beam entrance to the sample compartment.

12.3 Using methylene chloride as the solvent blank in a micro-cuvette, adjust the instrument to zero absorbance.

12.4 Calibrate the system daily as described in Section 7.

12.5 Determine the final volume of extract with a syringe and place sample in a micro-cuvette. Record the absorbance measurement.

12.6 If the measured absorbance exceeds the linear working calibration (approximately 0.35 absorbance units), dilute the extract and reanalyze.

12.7 Obtain fluoranthene equivalents (μg/mL) using the previously determined calibration curve of absorbance versus concentration of fluoranthene.

12.8 Calculate fluoranthene equivalents (μg/L) using the formula presented in Section 13.

12.9 If a wastewater is known to contain primarily one PAH compound (other than fluoranthene) the instrument may be calibrated with the appropriate reference standard so that concentration is given in equivalents of the compound of interest. However, if the PAH composition of the sample is unknown, fluoranthene must be used as the reference standard to ensure comparability of interlaboratory data.

13. CALCULATIONS

13.1 Determine the concentration of fluoranthene equivalents in the sample and the process blank.

13.1 Using the calibration curve of absorbance versus concentration of fluoranthene, determine fluoranthene concentration to the absorbance measurement obtained for the sample. The concentration of fluoranthene equivalents in the sample can be calculated from Equation 1:

$$\text{Concentration, } \mu g/L = \frac{C_A \times V_F}{V_S} \times 1.5 \qquad (1)$$

where:

C_A = calculated concentration in terms of fluoranthene equivalents in the extract (µg/mL)

1.5 = correction for fact 2/3 extract was analyzed

V_F = volume of final extract (mL)

V_S = volume of water extracted (L).

13.2 Subtract the PAH concentration value of the process blank (reagent) water processed in an identical manner as the samples) from the sample concentration in order to obtain the final result.

13.3 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.4 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits established in Section 8.4, data for that sample set must be labeled as suspect.

14. METHOD PERFORMANCE

14.1 Method detection limits - The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero (3). The MDL values obtained for total PAH in various water samples are given in Table B-2 (11).

14.2 This method has been tested for linearity of recovery (11) from spiked reagent water and has been demonstrated to be applicable over the concentration range from 2 x MDL to 100 x MDL. Representative data are given in Table B-4.

14.3 In a single laboratory (Battelle Columbus Laboratories), using spiked wastewater samples, the average recoveries presented in Table B-2 were obtained. Triplicate sample aliquots were analyzed at each spike level. The standard deviation of the percent recovery is also included in Table B-2.

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TABLE B-1. TOTAL UV ABSORPTION DATA FOR PRIORITY POLLUTANT PAHs

	Apparent Molar Absorptivity $\bar{\varepsilon}$	Molar Absorptivity Ratio a_I (a)
Naphthalene	1,800	0.29
Acenaphthene	1,800	0.29
Acenaphthylene	2,900	0.48
Fluorene	2,800	0.46
Anthracene	3,600	0.59
Phenanthrene	4,900	0.80
Pyrene	8,800	1.4
Fluoranthene	6,100	1.0
Benzo(a)anthracene	14,300	2.3
Chrysene	8,600	1.4
Benzo(a)pyrene	17,700	2.9
Benzo(b)fluoranthene	15,200	2.5
Benzo(k)fluoranthene	14,400	2.4
Dibenzo(a,h)anthracene	18,600	3.0
Benzo(ghi)perylene	17,000	2.8
Indeno(1,2,3-c,d)pyrene	17,300	2.8

UV Conditions: UV Spectrophotometer - Perkin-Elmer Model 55
Filter - Corning Number 7-54 Bandpass Filter
Concentration of PAH Standard Solutions - 10^{-5} M
Solvent - Methylene Chloride
Light Path Length - 10 mm

(a) Relative to fluoranthene.

TABLE B-2. SINGLE OPERATOR ACCURACY AND PRECISION

Water Type	Total PAH Spike Level (µg/L)	Average Percent Recovery ± RSD	Number of Analyses	Calculated MDL
Reagent Water	18 (27)[a]	96 ± 20[b]	3	ND
Reagent Water	3.6 (5.5)	99 ± 8	3	ND
Reagent Water	3.6 (5.5)	105 ± 8	7	3.5
POTW Effluent	36 (55)	76 ± 4	3	ND
POTW Effluent	3.6 (5.5)	92 ± 13	3	ND
Coking Effluent	36 (55)	78 ± 5	3	ND
Coking Effluent	3.6 (5.5)	97 ± 15	3	ND
Coking Effluent	3.6 (5.5)	82 ± 22	7	3.1
Refinery Effluent	36 (55)	84 ± 9	3	ND
Refinery Effluent	3.6 (5.5)	135 ± 32	3	ND
Refinery Effluent	3.6 (5.5)	135 ± 10	7	4.9

(a) Values in parenthesis are spike levels in terms of fluoranthene equivalents.

(b) Recovery values calculated using fluoranthene equivalent spike level.

ND = Not determined.

RSD = Percent relative standard deviation.

TABLE B-3. DATA FOR FLUORANTHENE CALIBRATION CURVE

Concentration µg/mL	Absorbance	Apparent Molar Absorptivity (a)
24.02	0.517	4348
12.01	0.340	5719
2.40	0.073	6139
1.20	0.031	5214

Conditions: UV Spectrometer - Perkin-Elmer Model 55B
Filter - Corning CS 9-54 Cutoff Filter
Solvent - Distilled in Glass Methylene Chloride
Light Path Length - 10 mm

(a) Apparent Molar Absorptivity $\bar{\varepsilon}$ = A/bc
A = Absorbance; b = Light Path Length, cm;
c = Concentration, mole/L

TABLE B-4. TOTAL PAH RECOVERY FROM REAGENT WATER AT VARIOUS SPIKE LEVELS

Spike Level ($\mu g/L$)(a)	Amount Found, ($\mu g/L$)	Percent Recovery ± SD
0	8	--
16	22	88 ± 22
64	65	91 ± 15
160	150	89 ± 1.4

(a) Spiked with equimolar mixture of 16 priority pollutant PAHs.

SD = Standard deviation.